

Badanie interfejsu molekula-metal za pomocą spektrometrii masowej jonów wtórnych



Jakub Ossowski

Praca doktorska wykonana pod kierunkiem:
dra hab. Piotra Cyganika

Zakład Fizyki Nanostruktur i Nanotechnologii

Instytut Fizyki

Uniwersytet Jagielloński

Kraków 2018

Wydział Fizyki, Astronomii i Informatyki Stosowanej
Uniwersytet Jagielloński

Oświadczenie

Ja niżej podpisany *Jakub Ossowski* (nr indeksu: 1039793), doktorant Wydziału Fizyki, Astronomii i Informatyki Stosowanej Uniwersytetu Jagiellońskiego oświadczam, że przedłożona przeze mnie rozprawa doktorska pt. *„Badanie interfejsu molekula-metal za pomocą spektrometrii masowej jonów wtórnych”* jest oryginalna i przedstawia wyniki badań wykonanych przeze mnie osobiście, pod kierunkiem dr hab. *Piotra Cyganika*. Pracę napisałem samodzielnie.

Oświadczam, że moja rozprawa doktorska została opracowana zgodnie z Ustawą o prawie autorskim i prawach pokrewnych z dnia 4 lutego 1994 r. (Dziennik Ustaw 1994 nr 24 poz. 83 wraz z późniejszymi zmianami).

Jestem świadom, że niezgodność niniejszego oświadczenia z prawdą ujawniona w dowolnym czasie, niezależnie od skutków prawnych wynikających z ww. ustawy, może spowodować unieważnienie stopnia nabytego na podstawie tej rozprawy.

Kraków, dnia 1.10.2018


.....
podpis doktoranta

*Niniejsza praca doktorska jest ukoronowaniem wielu lat pracy badawczej
pod opieką mojego promotora,
doktora habilitowanego Piotra Cyganika.*

*Chciałbym bardzo serdecznie podziękować dr hab. Piotrowi Cyganikowi
za cierpliwość i wyrozumiałość jaką wykazywał wobec mnie,
za włożony trud i wysiłek, dzięki któremu doszedłem do tego punktu
oraz za wiedzę, którą sukcesywnie mi przekazywał będąc przez cały ten czas prawdziwym
szefem, mentorem i przyjacielem.*

Spis treści

1. Forma pracy doktorskiej oraz opis indywidualnego wkładu autora	3
2. Problem badawczy podejmowany w pracy doktorskiej	5
3. Zarys kontekstu naukowego pracy doktorskiej	10
4. Krótki opis badań składających się na pracę doktorską	17
4.1 Oscylacje energii wiązań	17
4.2 Zamiana podłoża Au(111) → Ag(111)	21
4.3 Zastosowanie zjawiska oscylacji energii wiązań	23
4.4 Termiczny SIMS	29
5. Podsumowanie	32
6. Bibliografia	36
7. Dodatkowe osiągnięcia	38
8. Przedruki artykułów składających się na pracę doktorską	40

1. Forma pracy doktorskiej oraz opis indywidualnego wkładu autora.

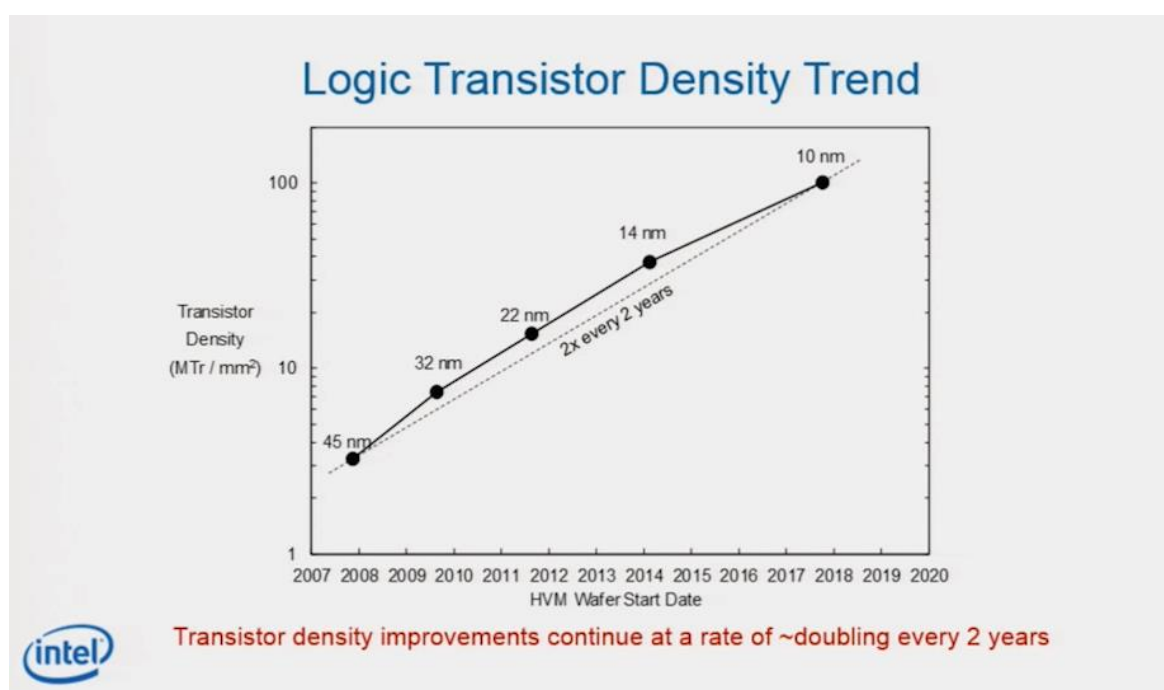
Na niniejszą pracę doktorską „Badanie interfejsu molekula-metal za pomocą spektrometrii masowej jonów wtórnych” składa się pięć artykułów opublikowanych w recenzowanych czasopismach naukowych o zasięgu międzynarodowym:

1. Jakub Ossowski, Jakub Rysz, Mariusz Krawiec, Dawid Maciazek, Zbigniew Postawa, Andreas Terfort, Piotr Cyganik „*Oscillations in the Stability of Consecutive Chemical Bonds Revealed by Ion-Induced Desorption*” *Angewandte Chemie International Edition*, **2015**, 54, 1336-1340
2. Jakub Ossowski, Tobias Waechter, Laura Silies, Martin Kind, Agnieszka Noworolska, Florian Blobner, Dominika Gnatek, Jakub Rysz, Michael Bolte, Peter Feulner, Andreas Terfort, Piotr Cyganik, Michael Zharnikov „*Thiolate versus Selenolate: Structure, Stability and Charge Transfer Properties*” *ACS Nano*, **2015**, 9, 4508-4526
3. Dominika Gnatek, Swen Schuster, Jakub Ossowski, Musammir Khan, Jakub Rysz, Simone Krakert, Andreas Terfort, Michael Zharnikov, Piotr Cyganik „*Odd-Even Effects in the Structure and Stability of Azobenzene-Substituted Alkanethiolates on Au(111) and Ag(111) Substrates*” *The Journal of Physical Chemistry C*, **2015**, 119, 25929-25944
4. Jakub Ossowski, Jakub Rysz, Andreas Terfort, Piotr Cyganik „*Relative stability of thiolate and selenolate SAMs on Ag(111) substrate studied by static SIMS. Oscillation in Stability of Consecutive Chemical Bonds*” *The Journal of Physical Chemistry C*, **2017**, 121, 459–470,
5. Jakub Ossowski, Giulia Nascimbeni, Tomasz Żaba, Elisabeth Verwüster, Jakub Rysz, Andreas Terfort, Michael Zharnikov, Egbert Zojer, Piotr Cyganik “*Relative Thermal Stability of Thiolate- and Selenolate-Bonded Aromatic Monolayers on the Au(111) Substrate*” *The Journal of Physical Chemistry C*, **2017**, 121, 28031-28042

Zgodnie z załączonymi oświadczeniami współautorów, w każdej z wymienionych pięciu prac autor był odpowiedzialny za przygotowanie próbek do badań i przeprowadzenie pomiarów metodą spektrometrii masowej jonów wtórnych, opracowaniu danych eksperymentalnych oraz pełną analizę otrzymanych wyników. Wkład autora w całkowity zakres prowadzonych badań odzwierciedla pozycja na liście autorów w poszczególnych publikacjach naukowych.

2. Problem badawczy podejmowany w pracy doktorskiej

Celem niniejszej pracy doktorskiej jest określenie możliwości wykorzystania spektrometrii masowej jonów wtórnych (Secondary Ion Mass Spectrometry – SIMS) do analizy stabilności interfejsu molekula-metal na przykładzie modelowych związków jakimi są samoorganizujące się monowarstwy organiczne (Self-Assembled Monolayers – SAMs). Wnioski płynące z pracy mogą zostać wykorzystane między innymi przy projektowaniu monowarstw monomolekularnych mających komercyjne zastosowanie w szeroko rozumianej elektronice molekularnej.



Rysunek 1. Na wykresie przedstawiono gęstość tranzystorów w procesorach firmy Intel w latach 2008-2018 r. Dodatkowo linią przerywaną zilustrowano trend prawa Moore’a. Rysunek pochodzi z [1].

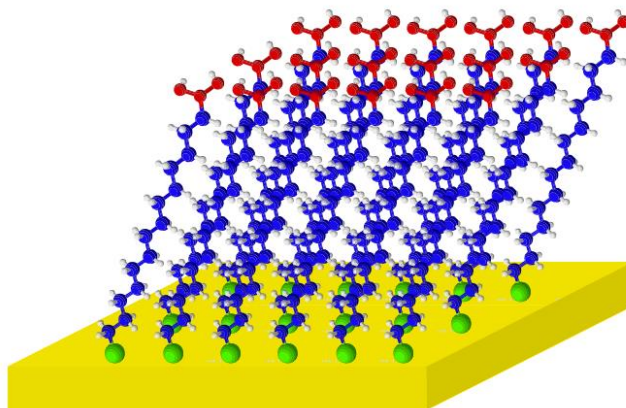
Poszukiwanie nowych kierunków rozwoju elektroniki jest naturalną konsekwencją empirycznego prawa Moore’a, które zakłada podwajanie się liczby układów scalonych mniej więcej co 2 lata^[2] (rys. 1). Przewidywany prawem Moore’a postęp w miniaturyzacji klasycznej, opartej na krzemie, elektroniki w pewnym momencie zatrzyma się, gdyż napotka na szereg ograniczeń wynikających zarówno z efektów kwantowych, które odgrywają tym większą rolę im mniejsze są wymiary wytwarzanych tranzystorów, jak i z opłacalności coraz bardziej skomplikowanej produkcji coraz mniejszych układów scalonych bazujących na krzemie. Sytuacja ta już dotyczy obecnie produkowanych od roku 2014 tranzystorów *Core M* firmy Intel

w technologii 14 nanometrów^[3]. Problem z jakim zetknęli się inżynierowie przy przejściu z wcześniejszej technologii 22 nm do obecnej 14 nm był nietrywialny – okazało się, że dotychczas stosowany proces fotolitograficzny w standardowej konfiguracji (naświetlanie laserem wafla krzemowego poprzez maskę) nie jest wystarczający do wytworzenia odpowiednio małych tranzystorów w tej technologii. Światło lasera ulega interferencji, jeżeli szczeliny maski położone są zbyt blisko siebie. Stąd Intel po raz pierwszy zastosował proces nazwany podwójnym naświetlaniem (ang. *Double-patterning*)^[4], w którym wykorzystuje się dwie różne maski z naprzemiennie umieszczonymi szczegółami, dzięki czemu uzyskuje się większą rozdzielczość litograficzną przy jednoczesnym uniknięciu niepożądanego interferencji wiązki laserowej. Niestety, nowy proces zastosowany przy fabrykacji układów scalonych opartych o technologię 14 nm jest zdecydowanie dłuższy od poprzedniego, co znajduje wyraźne odbicie w kosztach produkcji. Jeszcze droższa będzie seria procesorów *Cannon Lake* firmy Intel^[5], których premiera zapowiedziana jest w II połowie 2018 roku. Do ich wytwarzania stosuje się proces wielokrotnego naświetlania (ang. *Multi-patterning*)^[6], który umożliwia kolejny krok na drodze miniaturyzacji, czyli produkcję układów scalonych w technologii 10 nm. Trudno powiedzieć jednak kiedy dokładnie zostaną wyprodukowane jeszcze nowsze procesory, jednak istnieją przypuszczenia, że rok 2036, z uwagi na efekty kwantowe, wyznacza granicę stosowalności prawa Moore’a^[7] i tym samym kończy erę miniaturyzacji konwencjonalnej elektroniki opartej na krzemie. Oznacza to, że potrzebne są nowe, alternatywne rozwiązania. Jednym z najbardziej obiecujących kierunków jest właśnie elektronika molekularna.

Pierwsze badania w dziedzinie elektroniki molekularnej zostały przeprowadzone w grupie prof. Hansa Kuhna na początku lat 70 ubiegłego wieku^[8]. W szczególności zostało zademonstrowane jak zmienia się przewodnictwo elektryczne przez cienką warstwę soli kadmowych wyższych kwasów karboksylowych w zależności od długości łańcucha alifatycznego. Otrzymano zależność eksponencjalnego spadku przewodnictwa wraz ze wzrostem długości molekuly budującej monowarstwę. W następnych latach rozpoczęto badania pojedynczych molekuł, co zapoczątkowała praca Avirama i Ratnera z roku 1974^[9]. Autorzy zasugerowali, że pojedyncza molekula może pełnić rolę urządzenia – w ich przypadku diody (prostownika) – oraz, że taki obwód elektryczny z jedną cząsteczką pomiędzy dwiema elektrodami może rzeczywiście zostać zrealizowany i doświadczalnie przeanalizowany. W tamtym okresie, była to teoria z pogranicza fantastyki naukowej i najnowocześniejszych osiągnięć technologicznych, jednak niewiele ponad 20 lat później taki pomiar z wykorzystaniem molekuly benzene-1,4-ditiolu stał

się faktem, a sama publikacja doczekała się przeszło 2800 cytowań^[10]. Sukces tej pracy zaowocował szeroko zakrojonymi badaniami naukowymi, które dostarczyły szeregu informacji o sposobie i mechanizmie przewodnictwa elektrycznego pojedynczych cząsteczek chemicznych. Zbadano wiele systemów o potencjalnym zastosowaniu jako tranzystory, przełączniki, elementy pamięci czy klasyczne bramki logiczne. Pomimo dużych starań, zdecydowana większość tego typu układów nigdy nie znalazła praktycznych zastosowań w komercyjnie stosowanej elektronice organicznej. Jedną z największych przeszkód na drodze komercjalizacji jest problem z podłączeniem obwodu rozmiarów pojedynczej molekule do objętościowej elektrody^[11]. W obecnym stanie pokonanie trudności związanej z realizacją takiego złącza znacznie przewyższa potencjalny zysk, jaki płynąłby z zastosowania elektroniki na pojedynczej molekułce. Dużo łatwiejsza w produkcji jest elektronika oparta na wielu molekułach, czego przykładem są szeroko rozpowszechnione organiczne diody świecące (OLED), stosowane chociażby w produkcji wyświetlaczy do smartfonów czy laptopów. W standardowym OLED zjawisko elektroluminescencji zachodzi w materiale organicznym, umieszczonym pomiędzy dwiema elektrodami, z których jedna jest przezroczysta dla światła widzialnego. Emisja światła w takim urządzeniu jest efektem rekombinacji elektronów i dziur, które są wstrzykiwane odpowiednio z katody i anody. Oznacza to, że elektron w metalicznej katodzie ma do pokonania barierę potencjału przy transferze z poziomu energii Fermiego metalu na poziom LUMO półprzewodnika organicznego. Badania doświadczalne dowiodły, że właściwości elektrody, a szczególnie interfejsu metal-półprzewodnik organiczny odgrywają kluczową rolę w wydajności, efektywności i żywotności organicznych diod świecących. Niedoskonałości na granicy faz pomiędzy molekułami a metalem skutkują zmniejszeniem adhezji organicznego filmu do katody, co z kolei zwiększa rezystywność złącza i może powodować powstawanie nieemisyjnych czarnych plam w urządzeniu oraz skracać jego żywotność. Rozwiązanie problemu jakości interfejsu metal - materiał organiczny, który zasadniczo występuje w całej elektronice organicznej, jest niezbędne do dalszego rozwoju nie tylko OLED, ale również całej gałęzi nauki.

Obiecującym kandydatem zdolnym poprawić jakość interfejsu metal-materiał organiczny są samoorganizujące się monowarstwy molekularne (SAMs, ang. *Self-Assembled Monolayers*)^[12-14]. SAMy (rys. 2) to uporządkowane quasi-dwuwymiarowe struktury monomolekularne, zbudowane z organicznych molekuł chemicznie związanych z



Rysunek 2. Schematyczne przedstawienie monowarstwy SAM.

nieorganicznym podłożem. Proces formowania monowarstwy jest zjawiskiem całkowicie spontanicznym, co stanowi aplikacyjną zaletę, gdyż do utworzenia SAMu nie jest potrzebny czynnik zewnętrzny. Pozostałymi zaletami monowarstw SAM w kontekście zastosowań, zwłaszcza w elektronice molekularnej są między innymi: i) łatwość preparatyki warstw; ii) możliwość zaprojektowania właściwości molekuly i następnie jej zsyntezowania; iii) grubość typowej monowarstwy jest rzędu 1-3 nm, a więc stosowanie tych układów nie zwiększa znacząco końcowych rozmiarów urządzenia. Jednakże struktury typu SAM są badane relatywnie od niedawna, stąd wiele problemów wciąż pozostaje otwartych, również tych o znaczeniu fundamentalnym. Jednym z nich jest dobór odpowiedniej grupy wiążącej chemicznie molekułę do metalu w taki sposób, aby powstające wiązanie chemiczne było zarówno stabilne termicznie, jak i zapewniało dobre przewodnictwo ładunku (elektrony/dziury) poprzez interfejs molekula-metal. Zrozumienie mechanizmu przewodnictwa elektronowego i jego powiązania ze stabilnością wiązań chemicznych na złączu metal-molekuła ma kluczowe znaczenie dla rozwoju całej dziedziny elektroniki molekularnej i wciąż pozostaje wyzwaniem zarówno dla badań doświadczalnych jak i obliczeń teoretycznych.

Wychodząc naprzeciw tym właśnie wyzwaniom, w niniejszej pracy doktorskiej podjęto następujące problemy badawcze: i) Zbadanie wpływu zmiany grupy wiążącej molekułę do podłoża na stabilność interfejsu molekula-metal ii) Zbadanie wpływu zmiany podłoża na stabilność interfejsu molekula-metal; iii) Zbadanie stabilności termicznej układu SAM w zależności od chemicznej budowy molekuly oraz typu podłoża oraz iv) Zbadanie wpływu stabilności wiązania molekula-metal na proces przewodnictwa złącza molekula-metal.

Należy podkreślić że projekt ten nie miał na celu zbadania wszystkich możliwych kombinacji interfejsu molekula-metal, co byłoby zresztą zadaniem zdecydowanie wykraczającym poza ramy tej pracy biorąc pod uwagę liczbę możliwych kombinacji. Dlatego obrano odmienną strategię takich badań - strategię polegającą na spójnej analizie kilku układów modelowych, których struktura została już wcześniej bardzo dobrze scharakteryzowana, tak aby móc przedstawić wnioski, które miałyby charakter bardziej ogólny i mogły być z powodzeniem zastosowane w projektowaniu nowych układów elektroniki molekularnej. Do analizy stabilności interfejsu molekula-metal w tych modelowych układach opartych na samoorganizujących się monowarstwach organicznych SAM wykorzystano oryginalne podejście bazujące na technice S-SIMS.^[15-19]

3. Zarys kontekstu naukowego pracy doktorskiej

Samoorganizacja jest autonomicznym procesem organizacji mniejszych elementów w większe układy i struktury bez udziału zewnętrznej siły^[20]. Jest szeroko rozpowszechniona w naturze, odpowiedzialna za pochodzenie wielu systemów zarówno ożywionych, jak i nieożywionych^[21], dla których charakterystyczną cechą jest to, że ich końcowe rozmiary są znacznie większe niż rozmiary budujących je komponentów. Natura tworzy skomplikowane systemy poprzez łączenie ze sobą mniejszych elementów - cząsteczek chemicznych, wśród których główną rolę odgrywają aminokwasy, nukleotydy, tłuszcze i cukry. Jeżeli ograniczymy definicję samoorganizacji do spontanicznego łączenia cząsteczek, należy podkreślić że kluczowym czynnikiem decydującym o powstaniu struktury jest koegzystencja oddziaływań kowalencyjnych (mocnych) oraz niekowalencyjnych (słabych) w różnych skalach długości i z porównywalnym wkładem energetycznym. W szczególności istotne są wiązania niekowalencyjne, wśród których wyróżnić można między innymi: oddziaływania wodorowe i koordynacyjne, van der Waalsa, elektrostatyczne, steryczne oraz hydrofobowe^[21]. Typowym przykładem samoorganizacji w naturze jest formowanie miceli i dwuwarstw lipidowych zbudowanych z molekuł amfifilowych, zwijanie oraz agregacja peptydów i protein, tworzenie struktur kwasów nukleinowych i ich kompleksów z białkami, jak również powstawanie membran komórkowych^[22]. Zajście opisanych procesów jest możliwe jedynie pod warunkiem odpowiedniej mobilności poszczególnych cząsteczek, gdyż układ dążąc do samoorganizacji, optymalizuje położenie osobnych komponentów w taki sposób, aby znaleźć się w minimum energetycznym. Stąd samoorganizacja najczęściej zachodzi w fazach ciekłych lub na płaskich powierzchniach, a środowisko w którym przebiega ten samorzutny proces odgrywa kluczową rolę poprzez modyfikowanie oddziaływań pomiędzy molekułami. W szczególności zastosowanie odpowiednio zaprojektowanych powierzchni może znacząco poprawić jakość otrzymywanych struktur redukując w nich naprężenia i defekty.

Potencjał wykorzystania właściwości chemicznie zaprojektowanych cząsteczek zainspirował badaczy do wykorzystania procesu samoorganizacji jako metody tworzenia większych funkcjonalnych układów poprzez budowanie ich z mniejszych elementów na poziomie molekularnym. Takie podejście nosi nazwę bottom-up (z dołu do góry) i jest przeciwieństwem podejścia top-down (z góry do dołu), czyli podejścia bazującego na zastosowaniu technik litograficznych szeroko stosowanych w dotychczasowej technologii fabrykacji procesorów. Wykorzystanie procesów samoorganizacji w elektronice jest zatem zupełnie odmienną

konceptcją tworzenia podstawowych elementów układów elektronicznych i otwiera zupełnie nowy rozdział tej gałęzi nauki.

Historia molekuł formujących się w wertykalnie zorientowaną i gęsto upakowaną monowarstwę na powierzchniach różnych materiałów poprzez adsorpcję z roztworu sięga roku 1946, kiedy to Zisman i inni^[23] zauważyli, że powierzchnia kolby stożkowej stała się oleofobowa po kontakcie z roztworem alkoholu arachidylowego rozpuszczonego w n-heksadekanie. W tamtym czasie potencjał tego typu planarnych struktur nie został jeszcze dostrzeżony, a sama publikacja spotkała się z umiarkowanym zainteresowaniem. Pod koniec lat 70 ubiegłego wieku, Sagiv utworzył monowarstwę ze zhydrolizowanych trichlorosilanów na powierzchni SiO_2 ^[24], a następnie jako pierwszy w tytule publikacji wykorzystał termin samoorganizujących się monowarstw molekularnych^[25]. Nuzzo i Allara kilka lat później pokazali, że tiole mogą zostać chemicznie zaadsorbowane na powierzchni złota z rozcieńczonego roztworu zawierającego organiczne molekuły disulfidów^[26]. Samoorganizujące się monowarstwy molekularne zbudowane z organicznych tioli chemicznie związanych z powierzchnią złota stały się najbardziej popularnymi warstwami SAM i zapoczątkowały gwałtowny rozwój badań nad tego typu układami, który z ogromnym sukcesem trwa do dziś. Obecnie, po kilku dekadach badań, samoorganizujące się monowarstwy molekularne definiuje się jako planarną (quasi-dwuwymiarową), krystaliczną strukturę zbudowaną z molekuł na odpowiednio dobranej powierzchni. Monowarstwa SAM powstaje poprzez utworzenie chemicznego wiązania pomiędzy molekułami i podłożem, a następnie w sposób całkowicie spontaniczny, w celu obniżenia energii całego układu, cząsteczki porządkują się i formują pojedynczą, wertykalną warstwę. Można wyróżnić trzy charakterystyczne części budujące monowarstwę SAM: i) grupa czołowa, która odpowiedzialna jest za wiązanie chemiczne z podłożem; ii) łańcuch węglowodorowy, będący swoistym „kręgosłupem” molekuły determinującym grubość warstwy SAM oraz oddziaływania międzycząsteczkowe konieczne dla samoorganizacji warstwy, iii) powierzchniowa grupa funkcyjna – określająca topografię, energię powierzchniową i funkcjonalność chemiczną powierzchni SAMu. Spontaniczny proces formowania takich układów wymaga od kilku do kilkunastu godzin i zachodzi najczęściej poprzez kontakt metalicznego podłoża złota lub srebra z molekułami organicznymi rozpuszczonymi w roztworze ciekłym lub w parach gazu^[27].

Odkrycie monowarstw SAM, a w szczególności scharakteryzowanie najbardziej klasycznego układu alkanotiole na powierzchni Au(111)^[12,28] otworzyło zupełnie nowy rozdział w fizykochemii powierzchni. Połączyło ze sobą badania nad nieorganicznymi powierzchniami z organicznymi molekułami tworząc tym samym układ, który odmienił sposób myślenia o funkcjonalizacji powierzchni metali za pomocą chemii organicznej. Decydującym motorem rozwoju badań nad monowarstwami SAM są ich szerokie perspektywy zastosowań w różnych dziedzinach nauki i techniki^[13]. Najwięcej emocji w kontekście aplikacyjnym budzi możliwość wykorzystania systemów SAM w szeroko rozumianej elektronice molekularnej. Pojęcie to jest obecnie związane nie tylko z elektroniką na pojedynczych molekułach, ale także rozciąga się na obszar zastosowania cienkich warstw i kryształów molekularnych. Niezależnie od tego, czy rozważa się urządzenia typu OLED^[29], OFET^[30], OPV^[31], czy też warstwy izolujące^[32], przełączniki^[33], prostowniki^[34] albo elementy pamięci^[35], samoorganizujące się monowarstwy molekularne w każdym wymienionym przypadku znajdują obecnie zastosowanie.

Utrzymanie tempa rozwoju badań nad SAMami jest silnie skorelowane z poznaniem podstawowego mechanizmu formowania się samych warstw i zasad rządzących interfejsem molekula-metal. Niestety, pomimo szeregu prac poświęconych tej tematyce, wiele zasadniczych problemów pozostaje wciąż nierozwiązanych, które w ocenie autora niniejszej pracy doktorskiej są kluczowe dla bliższego poznania natury samoorganizujących się monowarstw molekularnych.

O sukcesie aplikacyjnym danego systemu rozstrzyga w dużej mierze zdolność do projektowania i kontrolowania jego właściwości fizyko-chemicznych. W przypadku monowarstw SAM istotny wpływ na parametry układu wywiera wciąż mało poznany mechanizm wiązania się molekuly organicznej z podłożem^[36,37]. Oddziaływanie to determinuje nie tylko siłę wiązania chemicznego decydującą o wysokości bariery potencjału na transport ładunku przez interfejs, ale również kierunek orientacji molekuly w przestrzeni. Pierwszymi SAMami najbardziej gruntownie przebadanymi w ujęciu eksperymentalnym były monowarstwy zbudowane ze wspomnianych molekuł alkanotiole na powierzchni Au(111). W ślad za pracami doświadczalnymi podążały prace teoretyczne, które rozważały sposób wiązania siarki do powierzchni złota. Zaproponowanych zostało wiele modeli geometrii adsorpcji S/Au(111), niestety nawet dla najprostszych układów metylotiole nie istnieją obliczenia jednoznacznie wyjaśniające zagadnienie, co jest spowodowane ograniczeniami samych metod teoretycznych^[38-40]. Brak przejrzystości dotyczy również obliczenia siły wiązania siarka – złoto w monowarstwach typu SAM. W tym przypadku energia zależy ściśle od geometrii wiązania

(wiele możliwości: bridge, top, fcc, hcp) jak również od długości i typu łańcucha węglowodorowego, z którego zbudowana jest molekula. W literaturze można znaleźć wartości energii wiązania prostych molekuł tiolowych do złota zawierające się w dość szerokim przedziale 1-2 eV. W świetle niewystarczających obliczeń teoretycznych, prace doświadczalne obrały kierunek empirycznego zbadania wpływu rodzaju grupy wiążącej molekuly do metalicznego podłoża na stabilność monowarstwy. W ramach tych doświadczeń zaproponowano zbadanie zmiany atomu wiążącego z siarki na selen, co wydaje się wyborem naturalnym, gdyż oba pierwiastki leżą w tej samej, XVI grupie układu okresowego, a więc mają zbliżone właściwości chemiczne. Niestety prace doświadczalne oraz teoretyczne analizujące wpływ podstawienia $S \rightarrow Se$ w grupie czołowej na stabilność wiązania do powierzchni^[41, 42] oraz na przewodnictwo^[43,44] złącza molekularnego dały wzajemnie sprzeczne odpowiedzi. Prawdopodobną przyczyną tego stanu rzeczy jest niewłaściwy dobór układów SAM jakie poddano badaniom. W przypadku zestawienia stabilności dwóch analogicznych SAMów, różniących się jedynie grupą wiążącą molekulę z podłożem, należy zadbać aby utworzone monowarstwy były w pełni analogiczne. Oprócz chemicznie analogicznych cząsteczek budujących SAM, molekuly muszą być upakowane na powierzchni podłoża z podobną gęstością oraz tworzyć podobną strukturę. Brak takiej strukturalnej zgodności porównywanych ze sobą warstw SAM jest przyczyną rozbieżności wyników^[42,45- 47], jakie otrzymano analizując stabilność monowarstw aromatycznych opartych na benzenotiolach (BS) oraz benzenoselenolach (BSe), w których pierścień benzenowy jest wiązany do powierzchni złota za pomocą, odpowiednio, atomu siarki lub selenu. Jak się okazuje, różnica w gęstości upakowania molekuł BS oraz BSe wynosi ponad 30%, co skutkuje kompletnie odmiennymi oddziaływaniami intermolekularnymi. Ponieważ stabilność układu SAM jest wynikiem zarówno oddziaływania molekuly z podłożem (tj. wiązanie S-Au lub Se-Au), jak i oddziaływania pomiędzy molekulami, to obserwowana w eksperymencie różnica pomiędzy tiolami i selenolami może być w sposób racjonalny powiązana ze stabilnością wiązania do podłoża jedynie w przypadku, gdy pozostałe oddziaływania intermolekularne są identyczne i nie wpływają na stabilność porównywanych układów.

Takie kryterium spełniają monowarstwy hybrydowych molekuł alifatyczno-aromatycznych stanowiących szereg homologiczny $BPnS(Se)$ o ogólnym wzorze $CH_3-(C_6H_4)_2-[CH_2]_n-S(Se)$, gdzie $n = 2-6$. Pokazano, że dla danej wartości parametru n monowarstwy zbudowane z tych molekuł na powierzchni Au(111) i Ag(111) mają analogiczną strukturę, co pozwala porównać bezpośrednio ich stabilność^[41,48- 50]. Ponadto w zależności od parzystości parametru n warstwy

te wykazują zmianę swojej struktury. Udowodniono, że na powierzchni Au(111) monowarstwy BPnS(Se) o nieparzystym n formują struktury o wyraźnie większej gęstości upakowania i bardziej pionowej orientacji molekuł względem podłoża Au(111). Przy zamianie podłoża z Au(111) na Ag(111) efekt ten staje się przeciwny tzn. większą gęstością upakowania i bardziej pionową orientacją molekuł względem podłoża charakteryzują się monowarstwy o parzystych wartościach parametru n . Odwrócenie efektu parzystości ze zmianą podłoża jest przypuszczalnie związane ze zmianą kąta wiązania podłoże-S(Se)-C, odpowiednio, z wartości $\sim 104^\circ$ na $\sim 180^\circ$ ^[48,51,52]. Biorąc pod uwagę podobieństwo struktur, jakie są tworzone przez monowarstwy BPn(S) oraz BPn(Se) na powierzchniach Au(111) oraz Ag(111) układy te można wykorzystać do analizy wpływu wiązania molekula-metal na stabilność monowarstw SAM. Takie badania z wykorzystaniem analizy stabilności monowarstw na proces wymiany innymi molekułami zdolnymi tworzyć SAMy przeprowadzono dla monowarstw BPnS(Se) na podłożu Au(111), wykazując większą stabilność monowarstw opartych na selenie^[41]. Analogiczne pomiary stabilności dla podłoża Ag(111) nie zostały przeprowadzone dla tego typu monowarstw. Badania jakie przeprowadzono dla innych układów SAM, które nie spełniają kryteriów wskazanych powyżej, wskazują na większą stabilność wiązania Ag-S w porównaniu do Ag-Se. Biorąc pod uwagę jednak niejednoznaczność wyników opartych na układach, które nie są strukturalnie podobne należy uznać, że kwestia ta pozostaje otwarta i wymaga dalszych badań, do przeprowadzenia których doskonale nadają się na przykład warstwy BPnS(Se)/Ag(111).

Porównanie przewodnictwa monowarstw SAM opartych na tiolach i selenolach również napotyka na poważne trudności. Po pierwsze należy podkreślić, że do tej pory przeprowadzone zostały tylko dwa eksperymenty bazujące na wykorzystaniu pomiarów STM, które przyniosły sprzeczne wyniki^[43,44]. Pomiary te bazowały na przewodnictwie mierzonym dla pojedynczych molekuł, a nie monowarstw i podobnie jak pomiary stabilności nie porównywały układów podobnych i dobrze określonych, co najprawdopodobniej jest przyczyną uzyskania sprzecznych wyników.

W podsumowaniu należy stwierdzić, że pierwszym krokiem do wykonania wiarygodnych pomiarów porównujących stabilność bądź przewodnictwo monowarstw SAM w funkcji ich wiązania do podłoża metalicznego jest wybranie dobrze scharakteryzowanych układów, dla których porównanie takie może dać miarodajne wyniki. Należy także podkreślić, że znalezienie takich modelowych układów nie jest proste i wymaga przeglądu wielu potencjalnych kandydatów. Kolejnym istotnym krokiem w kierunku przeprowadzenia takiej analizy jest

wykorzystanie odpowiednich metod badawczych, które pozwoliłyby na zbadanie stabilności wiązania molekuł do powierzchni w monowarstwie SAM, a następnie skorelowanie tych wyników z pomiarami przewodnictwa.

W tego typu badaniach stabilności najczęściej wykorzystywaną techniką, jest termicznie programowana desorpcja (TPD lub TDS). Stanowi ona jedną z podstawowych metod chemii analitycznej polegającą na analizie par materiału desorbowanego z próbki wraz ze wzrostem jej temperatury. Klasyczny układ do termicznej desorpcji zawiera układ post-jonizacyjny na bazie wiązki elektronowej lub laserowej, za którym znajduje się kwadropolowy spektrometr masowy umożliwiający detekcję desorbowanych cząstek o zadanej masie. Niestety, dużą wadą rozwiązania z post-jonizacją jest niska wydajność procesu, jak również częsta fragmentacja większych obiektów organicznych, co skutkuje powstawaniem artefaktów w widmie masowym. Dodatkowo detektory kwadropolowe mają typowy zakres detekcji obiektów do kilkuset jednostek masowych, co zazwyczaj wyklucza analizowanie cięższych molekuł organicznych.

Ograniczenia w detekcji masowej można pokonać stosując technikę spektrometrii masowej jonów wtórnych (SIMS), która stała się jedną z fundamentalnych technik badawczych powierzchni, głównie jako niedoścignione narzędzie w analizie składu chemicznego cienkich warstw organicznych czy obrazowaniu struktur biologicznych^[53-58]. SIMS jako metoda pomiarowa wydaje się być bardzo obiecującym narzędziem do analizy energii wiązań chemicznych na interfejsie molekula-metal w monowarstwach SAM. Spośród całej różnorodności innych technik badawczych, SIMS wyróżnia się: i) największą czułością ze wszystkich technik analitycznych (wykrywa zmiany w składzie chemicznym próbek poniżej 1 pbb(!)); ii) bezkonkurencyjnym stosunkiem sygnału do szumu; iii) Nielimitowanym zakresem masowym^[59]. Ponadto ogromną zaletą SIMSu jest pikosekundowa skala czasowa zjawisk jakie zachodzą po uderzeniu pocisku w tarczę. W tak krótkim czasie bombardowany układ nie jest w stanie dysypować przetransferowanej z pocisku energii, a więc nie relaksuje i nie zmienia się w czasie pomiaru. Z taką sytuacją mamy do czynienia szczególnie w reżimie statycznym SIMS (S-SIMS), gdy każdy padający jon uderza w nienaruszony, dziewiczy obszar tarczy. Jest to zupełnie inna koncepcja pomiarowa w porównaniu do klasycznych metod próbujących zrywanie wiązań chemicznych. W przypadku standardowej desorpcji zarówno temperaturowej jak i elektrochemicznej, czynnik zewnętrzny przykładany jest globalnie do całej próbki, a czas pomiaru często sięga godzin. W tak długim okresie czasu układ może ewoluować, przechodzić do innych faz zwłaszcza w przypadku monowarstw SAM^[60], a wtedy otrzymywana informacja

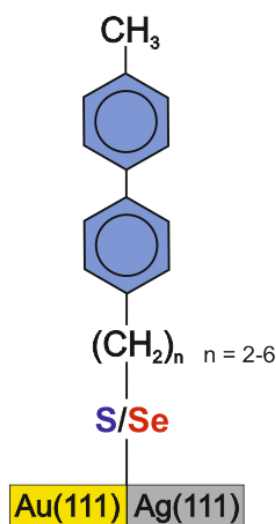
pochodzi z innego systemu niż pierwotnie wzięty do badań. W przypadku SIMSu problem ten nie istnieje.

Dotychczasowe badania struktur SAM za pomocą S-SIMSu skupiały się na procesie formowania struktur na różnych podłożach^[61-63], degradacji i uszkodzeń pod wpływem rozmaitych czynników^[64,65], czy też analizie stopnia metalizacji powierzchni monowarstwy SAM^[66]. W literaturze brak jest jednak prac w których technika ta byłaby wykorzystana do analizy stabilności interfejsu metal-molekuła organiczna, a tym bardziej w kontekście systemów SAM. W ostatnich latach zaproponowano połączenie techniki SIMS z pomiarami TDS uzyskując unikalne połączenie spektrometrii masowej jonów wtórnych z temperaturowo programowalną desorpcją. TP-SIMS jest techniką pozwalającą na analizę powierzchni próbki w funkcji temperatury z czułością i zakresem masowym SIMSu, czyli znacznie przewyższającym standardowe układy do termicznej desorpcji. Inną bardzo ważną zaletą techniki TP-SIMS jest możliwość określenia energii desorpcji jako sumy energii wiązania chemicznego i desorpcyjnej energii aktywacji. Niestety aparatura w takiej konfiguracji jest rzadko spotykana. W przypadku monowarstw SAM technika ta została wykorzystana jak dotąd tylko w kilku pracach^[59,67].

4. Krótki opis badań składających się na pracę doktorską

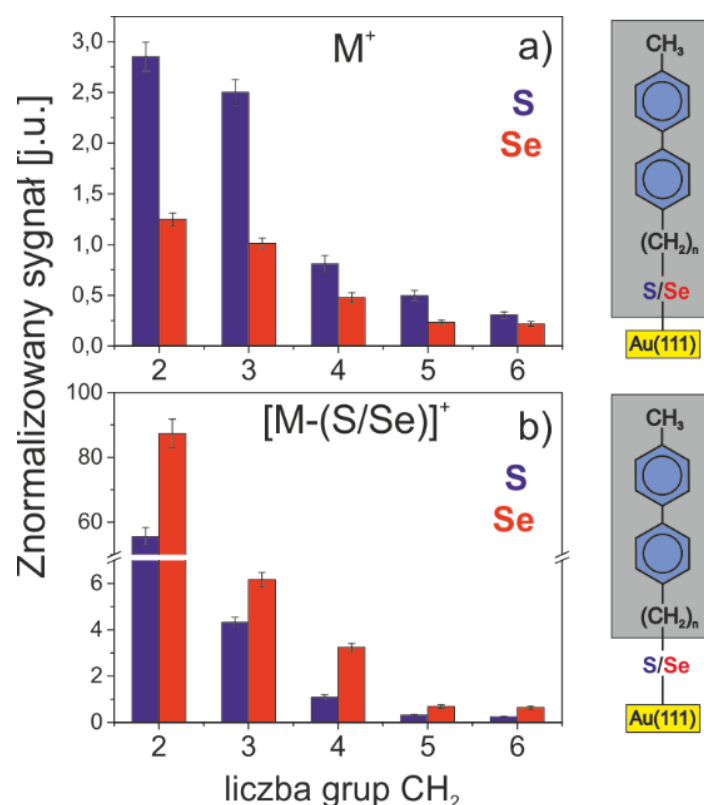
Wszystkie pomiary przeprowadzone w ramach pracy doktorskiej wykonano na spektrometrze masowym jonów wtórnych (ToF-SIMS V, ION-ToF GmbH) w laboratorium Zakładu Inżynierii Nowych Materiałów, natomiast preparatykę próbek wykonano w Zakładzie Fizyki Nanostruktur i Nanotechnologii na Wydziale Fizyki, Astronomii i Informatyki Stosowanej Uniwersytetu Jagiellońskiego.

4.1 Oscylacje energii wiązań



Rysunek 1. Molekuły wykorzystane w badaniach. Parametr n oznacza liczbę grup metylowych w łańcuchu alifatycznym

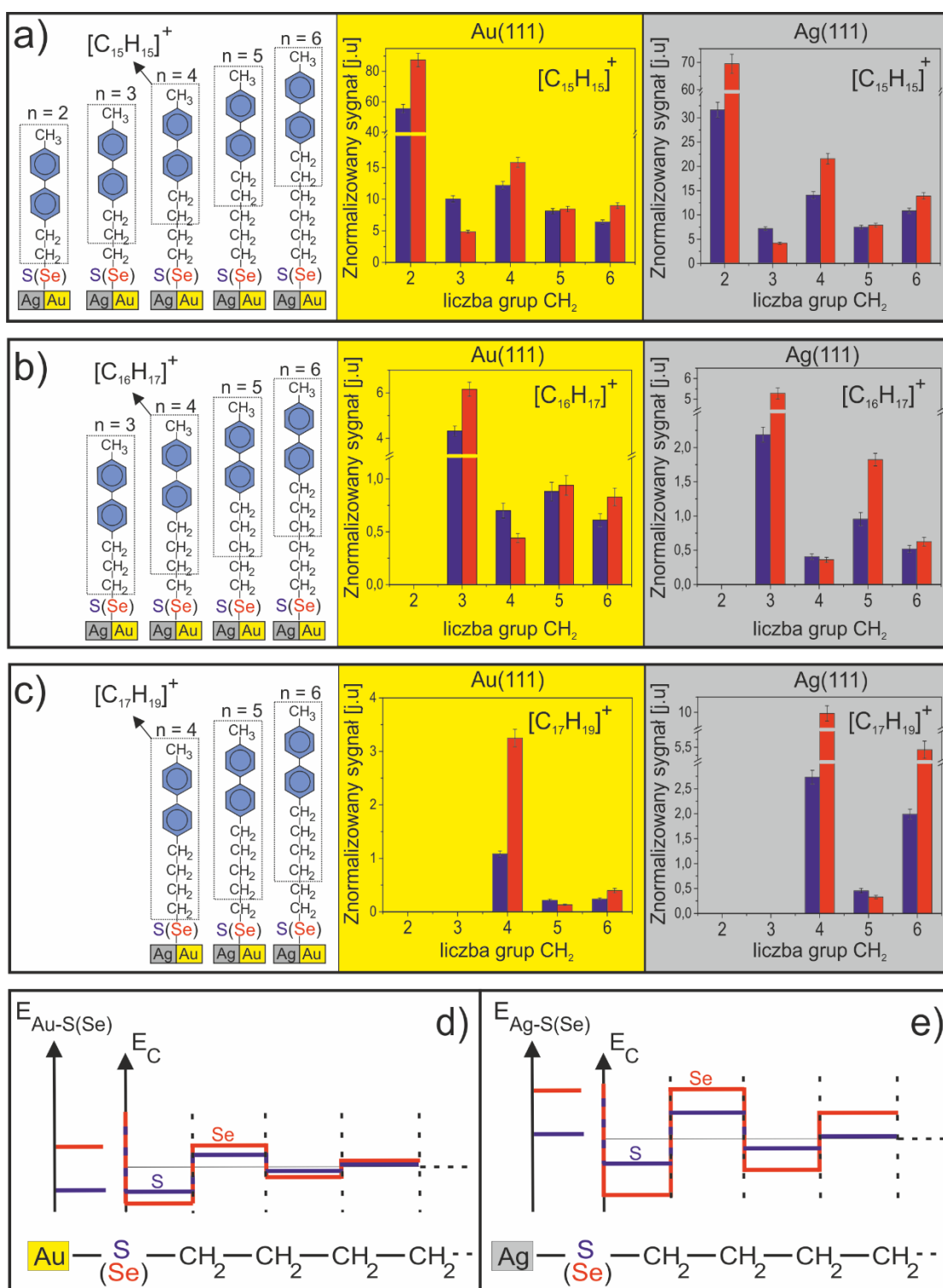
Pierwsze przeprowadzone pomiary składające się na niniejszą pracę doktorską miały pierwotnie za zadanie sprawdzić, czy SIMS jest techniką zdolną do ujawnienia różnic w stabilności bliźniaczych monowarstw, zbudowanych z chemicznie tożsamyh molekuł, różniących się atomem wiążącym cząsteczkę do podłoża i tworzących niemalże identyczne struktury SAM. Do realizacji tego zadania zostały ściśle wyselekcjonowane molekuły z szeregu homologicznego BPnS/Au(111) ($\text{CH}_3\text{-[C}_6\text{H}_4\text{]}_2\text{-[CH}_2\text{]}_n\text{-S/Au(111)}$, $n = 2 - 6$) oraz ich selenolowe analogi BPnSe/Au(111) ($\text{CH}_3\text{-[C}_6\text{H}_4\text{]}_2\text{-[CH}_2\text{]}_n\text{-Se/Au(111)}$, $n = 2 - 6$) przedstawione na rysunku 3. Monowarstwy SAM uformowane z obu typów molekuł tioli i selenoli zostały w ostatnich latach na tyle gruntownie przestudiowane, że obecnie uważane są za układ



Rysunek 2. Analiza danych SIMS. Wykresy (a) i (b) prezentują znormalizowaną emisję odpowiednio kompletnej molekuly (M^+) i fragmentu bez siarki/selenu ($M-(S/Se)^+$) z monowarstw BPnS (niebieskie słupki) oraz BPnSe (czerwone słupki).

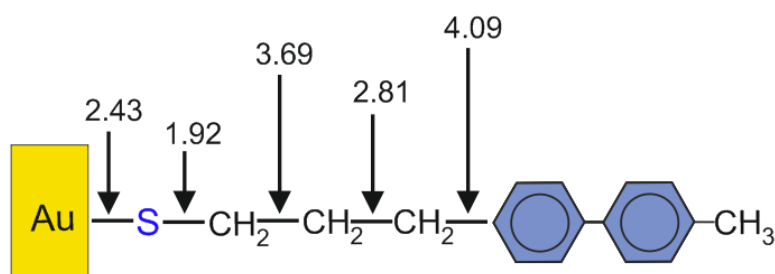
modelowy^[48,49,51,52,68-71]. Kluczowym aspektem tych pomiarów było porównanie ze sobą dwóch rodzin molekuł formujących układy SAM, a nie jedynie dwóch pojedynczych monowarstw. Pozwoliło to na szerszej zakrojonej analizie porównawczą, dzięki której zaobserwowano efekt będący motywem przewodnim publikacji otwierającej przewód doktorski.

Badania wstępne skupiły się na emisji kompletnej cząsteczki, czyli przerwaniu wiązania chemicznego Au-S lub Au-Se (rys. 4a), które jest kluczowym ogniwem w interfejsie molekula-metal i uznane zostało za decydujące w kontekście stabilności całej monowarstwy SAM. Wyniki przeprowadzonych pomiarów pokazały, że emisja kompletnej molekuly (M^+) jest znacznie silniejsza z monowarstw BPnS/Au(111) niż BPnSe/Au(111) (dla każdego $n!$), co jednoznacznie wskazuje na słabsze wiązanie Au-S w porównaniu do Au-Se. W kolejnym kroku analizie poddano fragment pozbawiony atomu wiążącego molekułę do podłoża ($M-S^+$) (rys. 4b). W tym przypadku okazuje się, że emisja węglowodorowego fragmentu molekuly pozbawionego atomu wiążącego (tj. siarki lub selenu) jest znacznie większa dla monowarstw selenolowych, co z kolei oznacza, że stosunkowo łatwiej jest przerwać wiązanie Se-C



Rysunek 5. Analiza danych SIMS. W prostokątach na schematach po lewej stronie panelów (a)-(c) zaznaczony jest fragment molekularny, którego emisja jest ściśle powiązana z przerwaniem odpowiedniego wiązania w cząsteczce. Po prawej stronie panelów przedstawiona jest znormalizowana emisja fragmentów $C_{15}H_{15}^+$ (a), $C_{16}H_{17}^+$ (b) oraz $C_{17}H_{19}^+$ (c) odpowiednio z podłoża Au(111) (żółte tło) oraz Ag(111) (szare tło). Niebieskie i czerwone słupki prezentują sygnały pochodzące odpowiednio z monowarstw BPnS i BPnSe. Panele (d) oraz (e) schematycznie podsumowują otrzymane wyniki odpowiednio z podłoża Au(111) oraz Ag(111): (i) większa energia wiązania Se-Au(Ag) w porównaniu do S-Au(Ag); (ii) większa energia wiązania S(Se)-Ag w porównaniu do S(Se)-Au; (iii) oscylacja energii kolejnych wiązań chemicznych wzdłuż łańcucha alifatycznego; (iv) efekt oscylacyjny zanika wraz ze zwiększaniem odległości od interfejsu molekula-metal; (v) amplituda oscylacji w przypadku monowarstw BPnSe jest większa względem BPnS, jak również amplituda jest większa w przypadku podłoża Ag(111) względem Au(111) dla obu szeregów homologicznych molekuł.

w porównaniu do wiązania S-C. Zjawisko to, można wytłumaczyć rozważając elektrony walencyjne siarki bądź selenu, które są zaangażowane w jednocześnie tworzenie dwóch wiązań chemicznych na interfejsie Au-S(Se)-C¹-C²-... . Jedno z tych wiązań jest z powierzchnią Au (wiązanie Au-S(Se)) a drugie z atomem węgla z pierwszej grupy metylowej łańcucha alifatycznego (wiązanie S(Se)-C¹). Większe zaangażowanie elektronów walencyjnych atomu siarki lub selenu w wiązanie z podłożem Au-S(Se) odbywa się kosztem mniejszego zaangażowania w wiązanie S(Se)-C¹. Można przypuszczać, że efekt ten będzie przenosił się na kolejne wiązania w tym szeregu, to znaczy słabsze wiązanie S(Se)-C¹ będzie skutkowało zwiększeniem stabilności kolejnego wiązania w szeregu, czyli wiązania C¹-C². Rozumowanie to prowadzi do powstania naprzemiennych zmian w stabilności kolejnych wiązań chemicznych wzdłuż łańcucha alifatycznego, czyli swoistych oscylacji (rys. 5). Oczywiście w miarę przechodzenia wzdłuż kolejnych wiązań łańcucha alifatycznego, mamy do czynienia z zanikaniem asymetrii w tym układzie molekularnym, a więc i amplituda tych oscylacji musi gasnąć, ponieważ źródłem oscylacji jest właśnie asymetria wiązań chemicznych. Ten efekt prowadzi zatem do zaniku oscylacji w miarę przesuwania się od interfejsu molekula-metal, który łamie symetrię translacyjną tego układu, w kierunku środka łańcucha alifatycznego gdzie symetria ta jest zachowana. W celu potwierdzenia tej hipotezy na gruncie analizy teoretycznej układu, nawiązano współpracę z dwiema grupami teoretycznymi. W pierwszym kroku w grupie Prof. Zbigniewa Postawy (Zakład Fizyki Nanostruktur i Nanotechnologii, FAIS UJ) przeprowadzono symulację procesu rozpylania warstw BP3S/Au na drodze symulacji dynamiką molekularną. Symulacje te miały na celu potwierdzenie, założenia, że obserwowane różnice w emisji kompletnej molekuly (M) oraz fragmentu bez atomu wiążącego (M-S) są rzeczywiście skorelowane ze zmianami w stabilności wiązań Au-S i S-C. W kolejnym kroku dr hab. Mariusz Krawiec z Uniwersytetu Marii Curie-Skłodowskiej w Lublinie posługując się



Rysunek 6. Obliczenia DFT wykonane dla molekuly w monowarstwie BP3S/Au(111) wraz z zaznaczonymi energiami (w eV) poszczególnych wiązań chemicznych. Rysunek pochodzi z pracy [15]

metodami Teorii Funkcjonałów Gęstości (DFT) przeprowadził obliczenia zarówno energii wiązań w monowarstwie BP3S/Au (rys. 6), jak i energii swobodnych molekuł: BP3SH, BPSeH oraz HS-(CH₂)₁₀-CH₃ potwierdzając, że oscylacja w stabilności kolejnych wiązań chemicznych jest bardziej ogólnym zjawiskiem, które nie tylko nie było do tej pory dyskutowane, ale nie zostało również wcześniej obserwowane na drodze eksperymentalnej^[15].

4.2 Zamiana podłoża Au(111) → Ag(111)

W kolejnym etapie rozwinięto dotychczasową analizę poprzez zbadanie struktur uformowanych z tych samych rodzin molekuł (BP_nS(Se), $n = 2 - 6$), chemisorbowanych do powierzchni Ag(111). Przeprowadzenie w pełni analogicznego pomiaru SIMS pozwoliło na bezpośrednie porównanie monowarstw BP_nS(Se)/Au(111) z BP_nS(Se)/Ag(111), a w szczególności sprawdzenie, czy efekt oscylacji energii kolejnych wiązań chemicznych w łańcuchu alifatycznym wystąpi również w układach na powierzchni srebra. Należy podkreślić fakt, że srebro jest materiałem wysoce pożądanym w przemyśle elektronicznym z uwagi na jego przewodnictwo właściwe [$1/\Omega \cdot m$], które dla srebra wynosi $61,39 \cdot 10^6$, dla złota natomiast $44,0 \cdot 10^6$, co stanowi o przewadze Ag nad Au w kontekście transportu elektronowego^[72].

W przypadku układów SAM zbudowanych z molekuł tworzących szereg homologiczny BP_nS(Se) ($n = 2 - 6$), występuje efekt parzystości, który ma swoje odzwierciedlenie w stabilności monowarstw. Mikroskopowe oraz spektroskopowe badania wykazały, że na powierzchni Au(111) gęściej upakowane i energetycznie lepiej zoptymalizowane są układy, w których łańcuch alifatyczny zbudowany jest z nieparzystej liczby grup metylowych ($n = 3, 5$) w porównaniu do parzystych homologów ($n = 2, 4, 6$). Zamiana podłoża z Au(111) na Ag(111) skutkuje odwróceniem efektu parzystości, w następstwie czego układami o większej stabilności i gęstości upakowania są te, w których łańcuch alifatyczny ma parzystą liczbę grup CH₂. Pierwsza część wyników SIMS przedstawiona w drugiej publikacji koncentruje się na emisji charakterystycznych dla układów SAM klastrów metaloorganicznych M₂Au⁻ oraz M₂Ag⁻ (gdzie M oznacza kompletną molekułę) będących swoistym „odciskiem palca” wiązania chemicznego pomiędzy molekułą i metalem. Analiza intensywności sygnału M₂Au(Ag) w funkcji parametru n jednoznacznie pokazała, że technika SIMS jest w stanie śledzić za subtelnymi zmianami w strukturze SAM i to pod dwoma różnymi kątami z punktu widzenia ich struktury. Po pierwsze zaobserwowano, że sygnały pochodzące z monowarstw tiolowych są bardziej intensywne od ich selenolowych odpowiedników (na tym samym podłożu), a różnica jest na poziomie jednego

rzędu wielkości. Wynik ten potwierdza eksperymenty wymiany przeprowadzone dodatkowo w tej pracy i świadczy o silniejszym wiązaniu Au(Ag)-Se w porównaniu do Au(Ag)-S. Po drugie, na powierzchni złota obserwowano silniejszą emisję klastrów metaloorganicznych w przypadku monowarstw BPnS(Se) zbudowanych z nieparzystych molekuł w porównaniu do parzystych, natomiast w przypadku powierzchni srebra efekt ten był odwrócony, co jest wyraźnym potwierdzeniem wspomnianego wcześniej efektu parzystości, którego faza zmienia się na przeciwną przy zmianie podłoża z Au(111) na Ag(111).

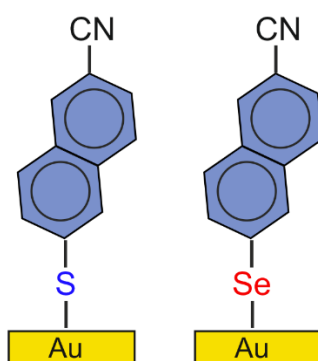
Kolejna część badań skupiła się na analizie sygnałów pochodzących od kompletnej molekuly oraz jej fragmentu pozbawionego siarki bądź selenu. Poprzez porównanie wyników uzyskanych dla warstw BPnS(Se) na tym samym podłożu (Au lub Ag) pokazano, że dużo łatwiej jest przerwać wiązanie S(Se)-C w porównaniu do wiązania zarówno Au-S(Se), jak i Ag-S(Se). Następnie analiza intensywności tych samych fragmentów molekularnych, ale dla układów osadzonych na różnych podłożach ujawnia, że wiązanie Au(Ag)-S jest wiązaniem słabszym w porównaniu do Au(Ag)-Se, przy jednoczesnym silniejszym wiązaniu S-C w porównaniu do Se-C, zarówno na złocie jak i na srebrze. Analiza tych danych pokazała również wyraźny efekt parzystości fragmentu M-S(Se) dla monowarstw utworzonych na powierzchni srebra i brak takiego zjawiska dla powierzchni złota. Można przypuszczać, że wynik ten wskazuje na znacznie większy wpływ efektu parzystości struktury monowarstw BPnS(Se) na stabilność wiązań chemicznych z podłożem Ag(111) niż z podłożem Au(111).

Końcowa i najważniejsza część badań polegała na sprawdzeniu, czy efekt oscylacji energii wiązań chemicznych na interfejsie molekula-metal zaobserwowany w monowarstwach osadzonych na powierzchni złota występuje również dla tych samych układów na powierzchni srebra. W tym celu przeprowadzono w pełni analogiczną analizę, a wszystkie wykresy zostały zebrane i przedstawione na rysunku 5.

Porównano ze sobą intensywności sygnałów jonów węglowodorowych ($[C_{15}H_{15}]^+$, $[C_{16}H_{17}]^+$, $[C_{17}H_{19}]^+$) emitowanych wskutek przzerwania odpowiednich wiązań pomiędzy atomami węgla w łańcuchu alifatycznym molekuł budujących monowarstwę SAM na obu typach podłoży. Analiza pokazała, iż wnioski wyciągnięte z poprzedniej pracy były prawidłowe. Okazuje się, że w monowarstwach na powierzchni srebra energia wiązań pomiędzy grupami metylowymi w łańcuchu alifatycznym również ma charakter oscylacyjny. Chociaż strukturalny efekt parzystości, mający swoje odzwierciedlenie w stabilności monowarstw, odwraca się przy zmianie podłoża z Au(111) na Ag(111), to zjawisko oscylacyjne się nie zmienia. Faza oscylacji jest identyczna jak przypadku Au(111), a amplituda wykazuje taki sam gasnący charakter. Maksymalną wartość uzyskuje przy samej powierzchni, a następnie oddalając się od interfejsu,

wraz z propagacją oscylacji wzdłuż łańcucha alifatycznego, amplituda oscylacji szybko maleje. Ponadto, niezależnie od doboru podłoża, amplituda jest większa w selenolowych monowarstwach w porównaniu do tiolowych. Następnie, w przypadku obu rodzin SAM dysproporcje energetyczne są większe dla molekuł osadzonych na powierzchni Ag(111) w porównaniu do Au(111), co jest spójne z wnioskami wyciągniętymi na podstawie analizy emisji kompletnej molekuły oraz fragmentu bez atomu wiążącego i oznacza, że cząsteczki mocniej wiążą się do powierzchni srebra. Należy podkreślić, że tak skrupulatna analiza możliwa była jedynie dzięki wykorzystaniu dwóch rodzin molekuł tworzących bardzo dobrze scharakteryzowane układy SAM na dwóch różnych podłożach, co w sumie pozwoliło udokumentować zjawisko oscylacji na podstawie bardzo spójnej i komplementarnej analizy 20 różnych monowarstw SAM^[16].

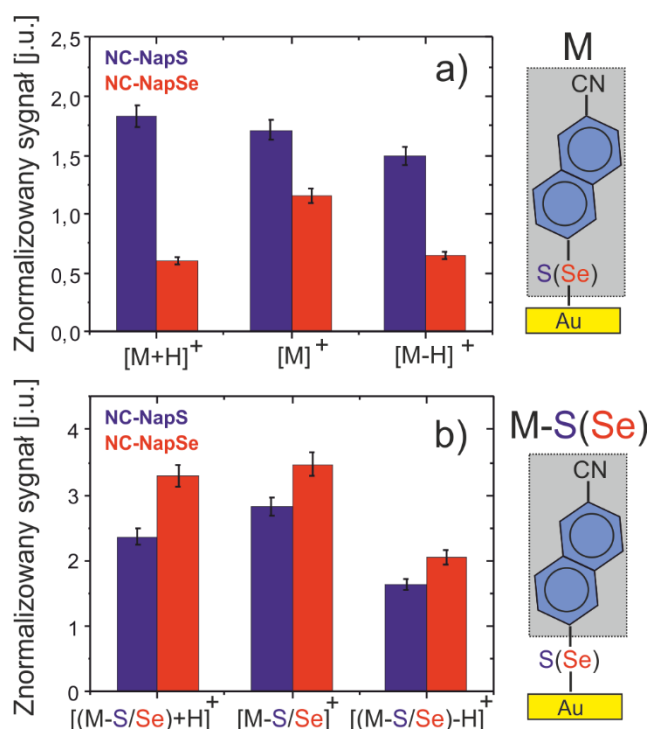
4.3 Zastosowanie zjawiska oscylacji energii wiązań



Rysunek 3. Molekuły wykorzystane w badaniach.

Jak wspomniano w rozdziale II, dużych trudności przysparza rozstrzygnięcie jaki wpływ na stabilność i przewodnictwo monowarstw SAM ma podstawienie $S \rightarrow Se$ w grupie czołowej. Z uwagi na fakt, że jakość interfejsu molekula-metal ma kluczowe znaczenie w kontekście przewodnictwa elektronowego, wspólnie z dwiema niemieckimi grupami badawczymi podjęto próbę rozwiązania tego problemu mającego charakter modelowy dla zrozumienia zasad budowy warstw SAM. Do badań wybrano molekuły 6-cyjanonaftaleno-2-tioli (NapS) oraz 6-cyjanonaftaleno-2-selenoli (NapSe) o wzorze $NC\equiv C_{10}H_6-S(Se)H$, z których uformowano monowarstwy SAM na powierzchni Au(111) (rys. 7). Za syntezę molekuł wraz z pomiarami elipsometrycznymi i refleksyjno-absorpcyjną spektroskopią w podczerwieni (IRRAS) odpowiedzialna była grupa prof. Andreasa Terforta z Uniwersytetu Goethego we Frankfurcie

nad Menem. Pomiary wysokorozdzielczej spektroskopii fotoelektronów (HRXPS), kątowno-rozdzielczej spektroskopii subtelnej struktury w pobliżu krawędzi absorpcji promieniowania rentgenowskiego (NEXAFS) oraz rezonansowej spektroskopii elektronów Augera (RAES) zostały wykonane przez grupę prof. Michaela Zharnikova z Uniwersytetu w Heidelbergu. Natomiast pomiary skaningowej mikroskopii tunelowej (STM), spektrometrii masowej jonów wtórnych (SIMS) oraz eksperymenty wymiany zostały wykonane przez grupę dr hab. Piotra Cyganika z Uniwersytetu Jagiellońskiego. Pomiary elipsometryczne, mikroskopowe oraz spektroskopowe (oprócz RAES) posłużyły do pełnego scharakteryzowania struktury monowarstw powstałych z obu typów molekuł. Otrzymane wyniki wyraźnie pokazały dwie bardzo zbliżone struktury, o podobnej gęstości upakowania molekuł i ich orientacji przestrzennej na powierzchni Au(111). Na tej podstawie można założyć, że ewentualne różnice w stabilności oraz przewodnictwie pomiędzy monowarstwami NapS/Au(111) i NapSe/Au(111) będą miały swoje źródło w interfejsie molekula-metal, czyli pozwolą na jednoznaczne wskazanie, który z atomów (S bądź Se) zapewnia układowi SAM lepszą stabilność i większe przewodnictwo elektryczne. Stabilność obu monowarstw zbadano w eksperymencie wymiany, którego idea polega na ekspozycji uprzednio uformowanego systemu SAM na roztwór zawierający molekuly innego rodzaju, również zdolne do tworzenia monowarstw. Wymiana zachodzi poprzez przerwanie pierwotnego wiązania molekula-metal i w jego miejsce utworzenie nowego wiązania przez molekułę z roztworu, przy czym w procesie tym faworyzowane jest wiązanie o większej energii. Za mniej stabilną uważa się zatem tę monowarstwę SAM, która wymieniła się w większym stopniu w porównaniu do swojego odpowiednika. W przypadku badań układów NapS/Au(111) i NapSe/Au(111), po upływie 120 godzin, monowarstwa selenolowa pozostała praktycznie nienaruszona (zaszła wymiana na poziomie 10%), podczas gdy monowarstwa tiolowa wymieniła się całkowicie. Wynik ten ma charakter zero-jedynkowy i jednoznacznie wskazuje wiązanie Au-Se jako zdecydowanie silniejsze w porównaniu do wiązania Au-S. Ponieważ dotychczasowe prace dostępne w literaturze^[43,44] sugerowały, na podstawie jedynie pośrednich eksperymentów, że silniejsze wiązanie molekuly do metalu jest gwarantem lepszego kontaktu elektrycznego i w efekcie większej wartości przewodnictwa układu, spodziewano się, że układ NapSe/Au(111) będzie lepiej przewodził prąd elektryczny w porównaniu do układu NapS/Au(111). W celu rozstrzygnięcia kwestii przewodnictwa przeprowadzono badania obu monowarstw metodą rezonansowej spektroskopii elektronów Augera. W technice RAES, co wyróżnia ją spośród innych metod badania przewodnictwa, złącze elektryczne nie jest tworzone i brak jest napięcia polaryzującego złącze, a zamiast pomiaru przewodnictwa określa się czas transferu elektronu



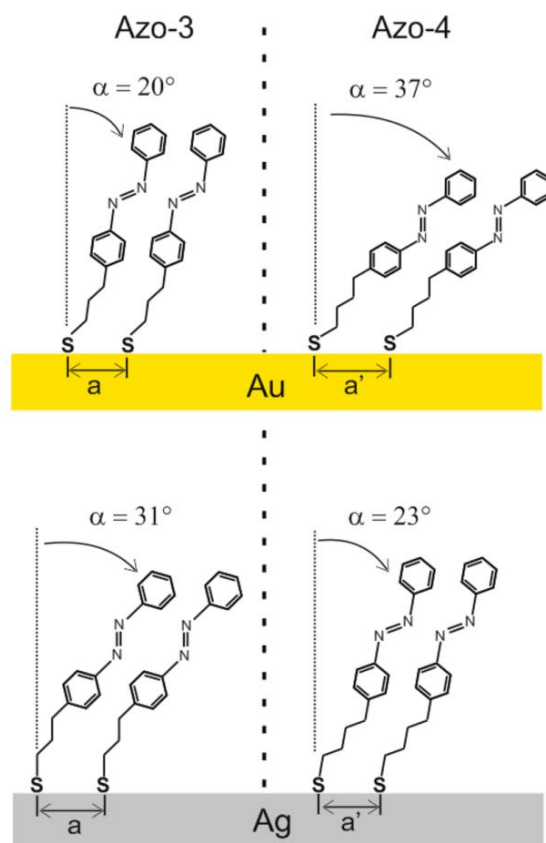
Rysunek 4. Analiza danych SIMS. Wykres (a) przedstawia znormalizowany sygnał emisji kompletnej molekuły z monowarstwy NC-NapS/Au(111) (niebieskie słupki) oraz NC-NapSe/Au(111) (czerwone słupki). Analogiczne dane dla emisji fragmentu pozbawionego siarki bądź selenu przedstawiono na wykresie (b).

do podłoża ze stanu wzbudzonego molekuły zlokalizowanego na jej swobodnym końcu, czyli na grupie funkcyjnej. W przypadku monowarstw NapS(Se)/Au(111) pomiar polegał na wzbudzeniu atomu azotu w grupie cyjanowej (CN), a następnie zmierzeniu czasu bezpromienistej deekscytacji układu poprzez przemieszczenie się elektronu z grupy CN wzdłuż całej molekuły do poziomu pasma przewodnictwa podłoża Au(111). Otrzymany wynik stał w sprzeczności z wcześniejszymi przypuszczeniami, bowiem zmierzony czas wyniósł 24 ± 4 fs niezależnie czy badana była monowarstwa NapS czy NapSe i na gruncie dotychczasowych eksperymentów był trudny do wytłumaczenia. Dla wytłumaczenia tego wyniku kluczowe okazały się pomiary SIMS, w których analizie poddano emisję kompletnej molekuły (przerwanie wiązania Au-S(Se)) i fragmentu molekularnego pozbawionego atomu grupy wiążącej (przerwanie wiązania S(Se)-C)) przedstawione na rysunku 8.

Wyniki jednoznacznie pokazały, że w badanych układach czysto aromatycznych warstw SAM selen wiąże się mocniej do złota niż siarka, przy jednoczesnym słabszym wiązaniu się selenu do węgla (w pierścieniu aromatycznym) względem analogicznego wiązania dla układu z siarką. Ten rezultat ponownie udowadnia, że zaangażowanie atomu w jedno z wiązań chemicznych

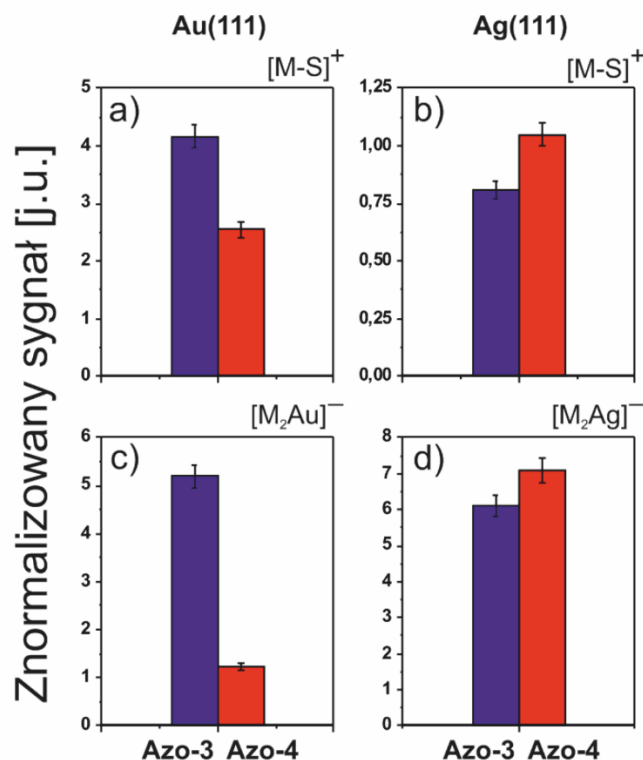
odbywa się kosztem energii drugiego wiązania. Wniosek ten może posłużyć do wytłumaczenia identycznej wartości przewodnictwa obu monowarstw, pomimo znacznie silniejszego wiązania Au-Se względem analogicznego wiązania Au-S. Dzieje się tak, ponieważ w trakcie procesu tunelowania transfer ładunku następuje poprzez oba sąsiadujące wiązania chemiczne (Au-S(Se)-C) i efekt sumaryczny tego procesu, z uwagi na kompensację silniejszego wiązania grupy czołowej do podłoża poprzez słabsze wiązanie tej grupy z resztą molekuly, prowadzi do podobnego rozkładu gęstości elektronów wzdłuż interfejsu molekula-metal dla obu typów atomów, co skutkuje bardzo podobną wartością przewodnictwa tunelowego przez złącze. Należy podkreślić, że hipoteza ta, choć sformułowana dla konkretnych w pełni aromatycznych układów SAM, ma naszym zdaniem znaczenie bardziej ogólne i może, na przykład, wytłumaczyć podobne przewodnictwo obserwowane eksperymentalnie dla warstw alkanotioli uformowanych na powierzchniach Au(111) i Ag(111)^[73], gdzie silniejsze wiązanie Ag-S w porównaniu do wiązania Au-S będzie kompensowane przez słabsze wiązanie S-C na podłożu Ag w porównaniu do podłoża Au.

Kolejną pracą, w której wykorzystano możliwość śledzenia energetyki wiązań chemicznych na interfejsie molekula-metal, były badania poświęcone analizie struktury SAM uformowanej z molekuł o wzorze $H_5C_6-N=N-C_6H_4-[CH_2]_n-SH$ ($n = 3, 4$). Ugrupowanie azobenzenowe ($H_5C_6-N=N-C_6H_4$) jest bardzo atrakcyjne z uwagi na swoje fotochromowe właściwości, pozwalające na indukowane światłem przełączanie pomiędzy stanami cis i trans, dzięki czemu potencjał aplikacyjny takich układów jest niezwykle szeroki. Jednakże dotychczas nie udało się otrzymać monowarstwy jednocześnie opartej na azobenzenie i spełniającej aplikacyjne wymagania, głównie z powodu zawady sterycznej, jaka uniemożliwia przełączanie molekuł w strukturach o dużej gęstości upakowania. W celu rozwiązania problemu, grupa prof. Andreasa Terforta zsyntezowała nowy typ molekuł, w których grupa azobenzenowa oddzielona jest od powierzchni elastycznym łańcuchem alifatycznym. Z kolei grupa Prof. Michaela Zharnikova wraz z grupą dr hab. Piotra Cyganika, scharakteryzowała właściwości monowarstw osadzonych zarówno na Au(111), jak i Ag(111), wykorzystując odpowiednio techniki HRXPS i NEXAFS oraz STM, SIMS i eksperyment wymiany. Dzięki zastosowaniu HRXPS, NEXAFS i STM określono gęstość upakowania molekuł na obu powierzchniach oraz ich przestrzenną orientację, co pozwoliło w pełni poznać strukturę monowarstwy SAM. Okazuje się, że na powierzchni Au(111) molekuły posiadające 3 grupy metylowe w łańcuchu alifatycznym (Azo3) tworzą gęściej upakowane i lepiej uporządkowane monowarstwy w porównaniu do molekuł z 4 grupami metylowymi (Azo4). Zależność ta, to nic innego jak efekt parzystości



Rysunek 5. Schematyczne przedstawienie efektu parzystości w monowarstwach Azo-3 oraz Azo-4 na podłożach Au(111) oraz Ag(111). Zaznaczono odpowiednie zmiany w wartości kąta odchylenia molekuly od normalnej do podłoża pomiędzy molekulami parzystymi i nieparzystymi. Rysunek pochodzi z pracy [19].

szerzej omówiony przy opisie badań nad molekulami BPnS(Se). Podobieństwo jest większe tym bardziej, że molekuly Azo3 i Azo4 na powierzchni Ag(111) tworzą monowarstwy wykazujące efekt parzystości o przeciwnej fazie względem powierzchni złota, czyli gęściej upakowany i lepiej uporządkowany jest układ SAM zbudowany z molekul Azo4 w porównaniu do Azo3 (rys. 9). Strukturalne różnice pomiędzy systemami SAM znajdują swoje odzwierciedlenie w eksperymencie wymiany, który próbuje stabilność wiązania molekuly do powierzchni, czyli wiązania Au(Ag)-S. Na podstawie eksperymentów wymiany zaobserwowano zależny od podłoża efekt parzystości w stabilności wiązania molekul do powierzchni, to znaczy pokazano, że łatwiej jest przerwać wiązanie molekula-Au(111) w monowarstwach Azo4 w porównaniu do Azo3, przy jednoczesnym silniejszym wiązaniu Azo4 do Ag(111) względem słabszego wiązania Azo3 do Ag(111). Ostatnią techniką wykorzystaną do badań nad omawianymi azobenzenowymi monowarstwami była spektrometria masowa jonów wtórnych, która jak pokazano wcześniej, jest zdolna wskazać słabsze i silniejsze wiązania chemiczne budujące cząsteczkę wchodzącą w skład monowarstwy SAM. Badania



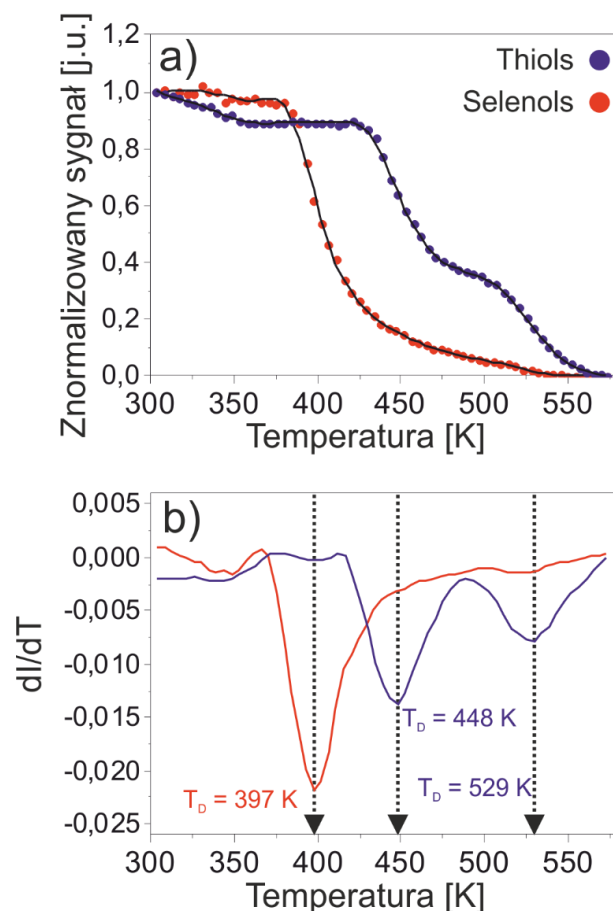
Rysunek 6. Analiza danych SIMS pochodzących z desorpcji monowarstw Azo-3 (niebieskie słupy) i Azo-4 (czerwone słupy) uformowanych na powierzchniach odpowiednio Au(111) (po lewej) oraz Ag(111) (po prawej). Wykresy (a) i (b) prezentują znormalizowaną emisję jonów $[M-S]^+$. Wykresy (c) i (d) prezentują znormalizowaną emisję jonów odpowiednio $[M_2Au]^-$ i $[M_2Ag]^-$.

techniką SIMS rozpoczęto od analizy emisji klastra M_2Au^- oraz fragmentu molekularnego pozbawionego siarki ($[M-S]^+$) z monowarstw na powierzchni złota (rys. 10). W obu wymienionych sygnałach, zdecydowanie większą intensywnością wyróżniają się jony pochodzące z układów SAM zbudowanych z molekuł Azo3. Detekcja jonu $[M-S]^+$ jest bezpośrednio związana z przerwaniem wiązania S-C, którego mniejsza stabilność wynika z większej stabilności wiązania Au-S i vice versa. Zatem większa intensywność molekularnego sygnału bez atomu siarki z monowarstw Azo3/Au(111) w porównaniu do Azo4/Au(111) świadczy o silniejszym wiązaniu w monowarstwie nieparzystej względem monowarstwy parzystej. Wynik ten jest w pełni zgodny z eksperymentem wymiany i demonstrowa efekt parzystości, który jest również widoczny w relatywnej intensywności emisji klastra M_2Au^- . Klastry typu molekula-metal są bardzo dobrze znane w analizie monowarstw SAM za pomocą techniki SIMS i stanowią dowód na istnienie uformowanego układu SAM. W przypadku klastra M_2Au^- intensywność emisji jest około 4-krotnie większa z monowarstw Azo3 względem Azo4, co można pośrednio skorelować z większą stabilnością wiązania Au-S i ponownie wskazać monowarstwę Azo3/Au(111) jako tę, która jest mocniej związana z powierzchnią w

porównaniu do Azo4/Au(111). Zamiana powierzchni ze złota na srebro powoduje, że wszystkie opisane wyżej relacje, łącznie z efektem parzystości, odwracają się. Dla monowarstwy Azo4/Ag(111) zaobserwowano większą intensywność sygnałów M_2Ag^- oraz $[M - S]^+$ w porównaniu do Azo3/Ag(111). Oznacza to, że silniejszym wiązaniem do powierzchni i jednocześnie słabszym wiązaniem S-C charakteryzuje się monowarstwa Azo4/Ag(111) względem Azo3/Ag(111), co jest w pełni zgodnie z eksperymentem wymiany i pozostałymi danymi spektroskopowymi. Dane SIMS pozwoliły jednoznacznie powiązać stabilność monowarstwy z jej strukturą i dopełniły charakterystyki systemów Azo3 oraz Azo4 na obu typach powierzchni metalicznych^[19].

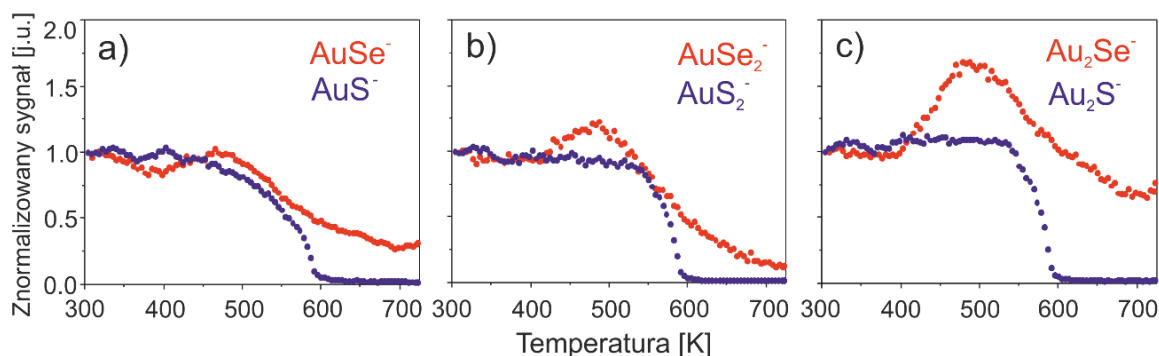
4.4 Termiczny SIMS

Wzorując się na opisanych przez grupę Prof. Alfreda Benninghova eksperymentach temperaturowo programowalnej spektrometrii masowej jonów wtórnych (TP-SIMS)^[59], wykonano pomiary stabilności termicznej dla gruntownie scharakteryzowanych i zbadanych pod kątem przewodnictwa i stabilności, układów naftalenotoli (NapS/Au(111)) i naftalenoselenoli (NapSe/Au(111)). Próbkę ogrzewano od temperatury pokojowej do 725K z liniowo narastającą temperaturą w tempie 3,75K/min. Śledzono ewolucję dwóch rodzajów sygnałów w funkcji temperatury (rys. 11). Pierwszym z nich był klaster molekula-metal w postaci M_2Au^- , który wykorzystano do analizy zmian stopnia pokrycia powierzchni molekułami w trakcie procesu termicznej desorpcji. Drugi fragment mający charakter nieorganiczny typu $Au_xS(Se)_y$ został wykorzystany do monitorowania zmian koncentracji atomu wiążącego molekułę do powierzchni w funkcji temperatury. Z przeprowadzonej analizy sygnału M_2Au^- wynika, że molekuly selenolowe desorbują w procesie jednoetapowym w temperaturze ~ 397 K, podczas gdy molekuly tiolowe desorbują w procesie dwuetapowym z dwóch różnych faz. Z pierwszej fazy o wysokiej gęstości pokrycia powierzchni desorbuje ok. 60% molekuł w temperaturze ~ 448 K, natomiast pozostałe 40% desorbuje z fazy niskiego pokrycia w temperaturze ~ 529 K. Korzystając z formuły Redhead'a^[75] oszacowano energię desorpcji, która dla naftalenoselenoli wynosi $E_D \sim 1,20$ eV przy $E_D \sim 1,35$ eV dla naftalenotoli (faza wysokiej gęstości), co daje różnicę $\Delta E_D \sim 0,15$ eV. Ponieważ obie monowarstwy są swoimi analogami, mają podobną gęstość upakowania i strukturę, możemy powiązać tę różnicę w energii desorpcji ze stabilnością termiczną interfejsu molekula-metal.



Rysunek 7. Analiza danych SIMS. Wykres (a) prezentuje emisję klastrow typu $[M_2-Au]^-$ znormalizowaną do intensywności emisji w temperaturze pokojowej w funkcji temperatury mierzonej dla monowarstw NapS/Au(111) (niebieskie punkty) oraz NapSe/Au(111) (czerwone punkty). Dwie linie ciągłe przedstawiają dopasowane wielomiany stopnia drugiego do danych pomiarowych, które następnie zróżniczkowano i zaprezentowano na wykresie (b). Czerwoną i niebieską linią zaznaczono zróżniczkowane wielomiany odpowiadające danym z monowarstw odpowiednio NapSe/Au(111) i NapS/Au(111). Wyznaczono charakterystyczne temperatury desorpcji odpowiadające minimom odpowiednich krzywych.

Dalszych informacji na temat stabilności termicznej tego interfejsu dostarczyła analiza fragmentów nieorganicznych (rys. 12). Dla Au_xSe_y zaobserwowano wzrost emisji w trakcie desorpcji monowarstwy, co wskazuje na bardziej efektywne przerywanie wiązania Se-C, w stosunku do wiązania Au-Se. W przypadku sygnału Au_xS_y poziom emisji nie wykazywał istotnych zmian w trakcie desorpcji monowarstwy, co oznacza bardziej zbalansowany proces przerywania wiązań Au-S i S-C, a zatem mniejszą różnicę w stabilności S-C i Au-S. W ten sposób pokazano, że główną przyczyną mniejszej stabilności termicznej monowarstw NapSe w porównaniu do NapS jest mniejsza stabilność wiązania Se-C w porównaniu do S-C. Oznacza to, że oszacowana powyżej różnica w energii desorpcji jest w głównej mierze powiązana z różnicą w stabilności Se-C i S-C, które są najsłabszymi wiązaniami na interfejsie molekula-metal.



Rysunek 8. Analiza danych SIMS dla monowarstw NC-Nap(S)Se/Au(111). Wykresy (a), (b), (c) prezentują emisję klastrow odpowiednio $\text{AuS}(\text{Se})^-$, $\text{AuS}(\text{Se})_2^-$, $\text{Au}_2\text{S}(\text{Se})^-$ znormalizowaną do intensywności emisji w temperaturze pokojowej w funkcji temperatury mierzonej dla monowarstw NC-Nap)/Au(111) (niebieskie punkty) oraz NC-NapSe/Au(111) (czerwone punkty).

Kolejnych informacji dostarczyła analiza sygnału $\text{Au}_x\text{S}(\text{Se})_y$ w zakresie wysokich temperatur tj. powyżej temperatury desorpcji monowarstwy ($T \sim 600 \text{ K}$). W przypadku AuS zaobserwowano gwałtowny spadek sygnału po zakończeniu procesu desorpcji molekuł, natomiast sygnał AuSe pozostawał widoczny w całym zakresie badanych temperatur tj. do $T = 725 \text{ K}$, co wskazuje na większą stabilność wiązania Au-Se w stosunku do Au-S i jest zgodne z wcześniejszymi wnioskami jakie wyciągnięto z opisywanej powyżej analizy procesów oscylacji stabilności kolejnych wiązań na interfejsie molekula-metal. Całą przedstawioną powyżej analizę SIMS uzupełniono dodatkowo pomiarami XPS, które były przeprowadzone przez innych członków zespołu naukowego, w celu potwierdzenia mniejszej stabilności termicznej monowarstw selenoli za pomocą innej techniki pomiarowej. Dodatkowo grupa teoretyków pod kierunkiem prof. Egberta Zojera z politechniki w Grazu wykonała obliczenia DFT struktury interfejsu molekula-metal w monowarstwach NapS(Se)/Au(111). Otrzymane rezultaty wskazały kilka możliwych, chociaż różnych od siebie, modeli adsorpcji molekuly na powierzchni złota i nie były w stanie jednoznacznie określić, który z nich jest realizowany w rzeczywistości. Jednak dzięki danym SIMS, które ujawniają wzajemne relacje energii wiązań w interfejsie NapS(Se)/Au(111), odrzucono większość wyników i wybrano 2 modele adsorpcji molekuł, w których występują adatomy Au. Tylko w przypadku modelu z adatomami obliczenia teoretyczne dały rezultaty zgodne z wynikami naszych prac doświadczalnych i ostatecznie zostały wspólnie opublikowane tworząc kompletny zestaw badań stabilności termicznej^[18]. W ten sposób pomiary SIMS po raz pierwszy pozwoliły na określenie nie tylko stabilności interfejsu molekula-metal ale także na stworzenie modelu struktury tego interfejsu, która jest wyjątkowo trudna do ustalenia zarówno w badaniach eksperymentalnych jak i symulacjach teoretycznych.

5. Podsumowanie

Na niniejszą pracę doktorską zatytułowaną „Badania interfejsu molekula-metal za pomocą SIMS” składa się 5 opublikowanych prac. Pierwsze dwie prace^[15,16] dzięki zastosowaniu techniki spektrometrii masowej jonów wtórnych, opisują nowo zbadane zjawisko oscylacji energii kolejnych wiązań chemicznych w molekułach formujących samoorganizujące się monowarstwach molekularne. Jest ono konsekwencją przerwania symetrii translacyjnej cząsteczki i stanowi o bardziej ogólnej zasadzie występującej w chemii organicznej, co zostało potwierdzone za pomocą obliczeń teoretycznych przeprowadzonych przez współpracowników. Ponadto zaprezentowane badania ujawniają, że natura efektu oscylacji wiązań jest niezależna od podłoża na którym uformowano monowarstwę, choć zbadane układy jednocześnie wykazują strukturalny efekt parzystości i jest on również widoczny za pomocą techniki SIMS. W ramach analizy efektu oscylacji można w szczególności porównać oraz wskazać który z atomów grupy czołowej (S bądź Se) tworzy stabilniejsze wiązanie do powierzchni, co jak wspomniano w rozdziale II, stanowiło „odwieczną” zagadkę w porównaniach monowarstw tiolowych z selenolowymi. Możliwość tę wykorzystano w pracy trzeciej tego cyklu^[17], w której badano monowarstwy SAM oparte na aromatycznym ugrupowaniu naftalenowym, które z uwagi na swoje przewodnictwo są bardzo obiecującym układem w kontekście aplikacyjnym. W eksperymencie wykonanym przez współpracowników zmierzono czas, jaki potrzebuje elektron na przetransferowanie się przez całą molekułę i wniknięcie do metalu. W obu przypadkach (zarówno monowarstw tiolowych, jak i selenolowych) otrzymano taki sam wynik. Z innych eksperymentów wykonanych również przez współpracowników wynikało, że monowarstwy selenolowe są zdecydowanie mocniej związane z powierzchnią w porównaniu do tiolowych odpowiedników, co nie pozwalało na wytłumaczenie identycznego przewodnictwa obu typów molekuł. Dopiero komparatywny eksperyment SIMS ujawnił, że choć selen faktycznie wiąże się mocniej do powierzchni względem siarki, to jednocześnie wiąże się słabiej do węgla w porównaniu do analogicznego wiązania siarki do węgla. Stąd sumaryczny efekt jest taki sam, co skutkuje identycznym czasem jaki potrzebuje elektron na transfer przez wiązania chemiczne C-S-Au(111) oraz C-Se-Au(111). W pracy czwartej^[19] ponownie wykorzystano możliwości badania stabilności wiązań chemicznych na interfejsie molekula-metal jakie stwarza technika SIMS. Analizowano monowarstwy SAM oparte na ugrupowaniu azobenzenowym, którego potencjał aplikacyjny wynika z możliwości łatwego przełączania pomiędzy stanami *cis* i *trans* za pomocą długości światła odpowiednio 320–350 nm (*cis* → *trans*) i 400–450 nm (*trans* →

cis). Analiza danych SIMS ujawniła istnienie efektu parzystości, który odwraca swoją fazę przy zamianie podłoża z Au(111) na Ag(111). Ponadto analiza intensywności emisji jonów molekularnych pozwoliła na wskazanie, który z układów SAM wiąże się mocniej do powierzchni, a otrzymany wynik w pełni koreluje się z efektem parzystości. W ostatniej, piątej pracy^[18], zastosowano technikę TP-SIMS w celu zbadania termicznej stabilności układów SAM, które zostały uprzednio gruntownie scharakteryzowane w pracy trzeciej. W przeprowadzonym eksperymencie najpierw porównano stabilność termiczną obu monowarstw i wyznaczono zarówno ich indywidualne energie desorpcji jak i różnicę. Na tym etapie określono, że wraz ze wzrostem temperatury układu najpierw desorbują selenole, a następnie tirole, co w pełni ilustruje względną stabilność obu monowarstw SAM. Następnie skoncentrowano się na analizie siarki i selenu, które zostają na powierzchni złota po odparowaniu części organicznej. Okazuje się, że w wysokich temperaturach siarka całkowicie odparowuje, podczas gdy selen zostaje na powierzchni złota tworząc z nią stop. Eksperymenty SIMS, poprzez określenie względnej stabilności wiązań Au-Se, Au-S, C-S oraz C-Se umożliwiły porównanie różnych modeli adsorpcji monowarstwy uzyskanych z obliczeń DFT i wskazanie, że jedynie modele adsorpcji, w których molekuły z siarką lub selenem wiążą się do podłoża poprzez adatomy złota dają wyniki zgodne z eksperymentami SIMS. W ten sposób wyniki SIMS nie tylko wsparły proponowany w ostatnich latach model adsorpcji tioli na powierzchni złota^[36,74] poprzez udział adatomów złota, ale również wskazały po raz pierwszy, że identyczny model może być stosowany także w przypadku selenoli.

Najprawdopodobniej spektrometria masowa jonów wtórnych, z uwagi na swoją niezwykle czułość, jest na chwilę obecną jedyną techniką, która pozwala na doświadczalne i precyzyjne śledzenie zmian w energetyce międzyatomowych wiązań chemicznych w monowarstwach SAM. Fakt ten może wydawać się sprzeczny z intuicją, biorąc pod uwagę, że w przeprowadzonych pomiarach wykorzystywany był pocisk Bi^+ o energii 30 000 eV, a badanym obiektem była miękka materia organiczna, w której bada się wiązania o energii rzędu 1-4 eV. Być może jest to powód, dla którego nikt wcześniej nie podjął się tak wysublimowanej analizy wiązań chemicznych i próbowano w tym celu wykorzystać inne metody badawcze. Jednakże dotychczasowe badania usiłujące próbować energię potrzebną na zerwanie wiązania chemicznego, nie były zdolne do precyzyjnego wskazania, które z wiązań zostało przerwane. Analiza danych SIMS jest w stanie dostarczyć informacji o stabilności danego wiązania chemicznego w odniesieniu do innego wiązania i to nie tylko w obrębie jednego badanego

układu, ale również pomiędzy nimi. SIMS w układzie z możliwością grzania analizowanej próbki staje się unikatowym narzędziem pozwalającym na określenie stabilności termicznej oraz obliczenie energii desorpcji korzystając z formuły Redhead'a^[75]. Dotychczasowo energię desorpcji otrzymywano ze standardowej analizy w układzie TDS, jednak jak wspomniano w rozdziale II, ta technika ma szereg ograniczeń wynikających chociażby z szybkości zbierania danych i zakresu analizowanych mas oraz sposobu jonizacji desorbowanych fragmentów organicznych. W przypadku SIMSu wspomniane problemy nie występują, gdyż w jednym czasie analizowany jest cały zakres masowy (do tysięcy jednostek atomowych), natomiast proces jonizacji, chociaż nie jest do końca poznany i kontrolowany, zachodzi w zupełnie inny sposób i inicjuje go uderzenie jonu w powierzchnię próbki. Warto także podkreślić, że SIMS jest stosunkowo popularną techniką analityczną, co stwarza możliwość prowadzenia analogicznych pomiarów przez wiele innych grup na świecie zajmujących się badaniami nanostruktur zarówno na poziomie podstawowym jak i technologicznym.

O sukcesie przedstawionych badań, w dużym stopniu zdecydowało odpowiednie dobranie molekuł tworzących monowarstwę SAM i różniących się od siebie jedynie grupą wiążącą, czyli atomem siarki bądź selenu. Jednak chemiczne podobieństwo cząsteczek stanowiło jedynie pierwszy etap, bowiem analizując dotychczasowe prace jest to warunek konieczny, ale nie wystarczający do porównania ze sobą uformowanych z tychże molekuł monowarstw. Kluczową kwestią w badaniach porównawczych stabilności interfejsu molekula-metal okazało się zestawienie ze sobą monowarstw, które mają praktycznie taką samą strukturę i gęstość upakowania. Dzięki temu wszystkie eksperymentalnie zaobserwowane różnice mają swoje źródło w interfejsie molekula-metal i wynikają z różnicy pomiędzy siarką i selenem. Ponadto bezpośrednie zestawienie ze sobą monowarstw zbudowanych z dwóch szeregów homologicznych molekuł pozwala na dużo szerszą analizę porównawczą układów SAM, aniżeli pojedynczych układów. Należy podkreślić ten fakt, bowiem bez tak szerokich badań nie udałooby się zaobserwować oscylacyjnego efektu w energiach wiązań chemicznych, który stanowi punkt wyjścia niniejszej pracy doktorskiej.

Reasumując, z pracy doktorskiej płyną dwa typy wniosków. Po pierwsze, SIMS jest techniką zdolną do analizy wiązań chemicznych na interfejsie molekula-metal w samoorganizujących się monowarstwach molekularnych. Ponadto metoda ta jest czuła na strukturalny efekt parzystości w monowarstwach SAM. Z kolei kombinacja TP i SIMS jest w stanie skutecznie śledzić ewolucję monowarstwy SAM w funkcji temperatury i tym samym określić jej termiczną stabilność, a z danych eksperymentalnych, przy użyciu równania Redhead'a^[75], można

wyliczyć energię desorpcji badanego układu. Po drugie, związanie się molekuly z podłożem powoduje zaburzenie równowagi energetycznej wiązań chemicznych w cząsteczce, które objawia się wystąpieniem oscylacyjnego efektu zmiany energii naprzemiennie występujących po sobie tychże wiązań. Analizując ten efekt, można oszacować względną stabilność badanych wiązań, w tym w szczególności wiązanie molekuly do powierzchni. Jednak, co pokazały badania, nie można na podstawie tylko jednego wiązania wnioskować o właściwościach układu molekula-metal w kontekście przewodnictwa elektronowego, wbrew temu co dotychczas sądzono.

6. Bibliografia

- [1] Bohr, M. „Integrated circuit scaling to 10 nm and beyond”, Intel, **2018**. (Dostęp: 01.10.2018, <https://www.youtube.com/watch?v=ApWOf6J858Y>)
- [2] G. E. Moore, *Electronics*, **1965**, 38, 114–117.
- [3] <https://www.intel.com/content/www/us/en/silicon-innovations/intel-14nm-technology.html> (Dostęp: 01.10.2018)
- [4] <https://newsroom.intel.com/newsroom/wp-content/uploads/sites/11/2017/03/Ruth-Brain-2017-Manufacturing.pdf> (Dostęp: 01.10.2018)
- [5] <https://newsroom.intel.com/news/intel-technology-manufacturing-day-china/> (Dostęp: 01.10.2018)
- [6] <https://newsroom.intel.com/newsroom/wp-content/uploads/sites/11/2017/03/Kaizad-Mistry-2017-Manufacturing.pdf> (Dostęp: 01.10.2018)
- [7] J.R. Powell, *Proceedings of the IEEE*, **2008**, 96, 1247–1248
- [8] B. Mann, H. Kuhn, *Journal of Applied Physics*, **1971**, 42, 4398–4405.
- [9] A. Aviram, M. A. Ratner, *Chemical Physics Letters*, **1974**, 29, 277–283.
- [10] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science*, **1997**, 278, 252–254.
- [11] R. F. Service, *Science*, **2003**, 302, (5645) 556–9.
- [12] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chemical Review*, **2005**, 105, 1103–1170
- [13] A. Ulman, *Chemical Review*, **1996**, 96, 1533–1554.
- [14] F. Schreiber, *Journal of Physics: Condensed Matter*, **2004**, 16, R881–R900.
- [15] J. Ossowski, J. Rysz, M. Krawiec, D. Maciążek, Z. Postawa, A. Terfort, P. Cyganik *Angewandte Chemie International Edition*, **2015**, 54, 1336–1340
- [16] J. Ossowski, J. Rysz, A. Terfort, P. Cyganik, *The Journal of Physical Chemistry C*, **2017**, 121, 459–470.
- [17] J. Ossowski, T. Wachter, L. Silies, M. Kind, A. Noworolska, F. Blobner, D. Gnatek, J. Rysz, M. Bolte, P. Feulner, A. Terfort, P. Cyganik, M. Zharnikov, *ACS Nano*, **2015**, 9, 4508–4526
- [18] J. Ossowski, G. Nascimbeni, T. Zaba, E. Verwüster, J. Rysz, A. Terfort, M. Zharnikov, E. Zojer, P. Cyganik, *The Journal of Physical Chemistry C*, **2017**, 121, 28031–28042
- [19] Dominika Gnatek, Swen Schuster, Jakub Ossowski, Musammir Khan, Jakub Rysz, Simone Krakert, Andreas Terfort, Michael Zharnikov, Piotr Cyganik, *Journal of Physical Chemistry C*, **2015**, 119, 25929–25944
- [20] G. M. Whitesides, B. Grzybowski, *Science*, **2002**, 295, 2418–2421.
- [21] S. Zhang, *Nature Biotechnology*, **2003**, 21, 1171–1178
- [22] S. Casalini, C.A. Bortolotti, F. Leonardi, F. Biscarini, *Chemical Society Reviews*, **2017**, 46, 40–71
- [23] W. C. Bigelow, D. L. Pickett, W. A. Zisman, *Journal of Colloid Science*, **1946**, 1, 513–538.
- [24] J. Sagiv, *Journal of the American Chemical Society*, **1980**, 399, 92–98.
- [26] R. Maoz and J. Sagiv, *Journal of Colloid and Interface Science*, **1984**, 100, 465–496
- [26] R.G. Nuzzo, D.L. Allara, *Journal of the American Chemical Society*, **1983**, 105, 4481–4483
- [27] D. K. Schwartz, *Annual Review of Physical Chemistry*, **2001**, 52, 107–137
- [28] C. D. Bain, G. M. Whitesides, *Journal of the American Chemical Society*, **1989**, 111, 7164–7175.
- [29] R. Partridge, *Polymer*, **1983**, 24, 733–782
- [30] H. Koezuka, A. Tsumura, T. Ando, *Synthetic Metals*, **1987**, 18, 699–704
- [31] B. de Boer, A. Hadipour, M. M. Mandoc, T. van Woudenberg, P. W. M. Blom, *Advanced Materials*, **2005**, 17, 621–625.
- [32] S. A. Di Benedetto, A. Facchetti, M. A. Ratner, T. J. Marks, *Advanced Materials*, **2009**, 21, 1407–1433.
- [33] V. Ferri, M. Elbing, G. Pace, M. D. Dickey, M. Zharnikov, P. Samori, M. A. Rampi, *Angewandte Chemie International Edition*, **2008**, 120, 3455–3457
- [34] J. R. Heath, *Annual Review of Materials Research*, **2009**, 39, 1–23
- [35] J. S. Lindsey, D. F. Bocian, *Accounts of Chemical Research*, **2011**, 44, 638–650.
- [36] H. Hakkinen, *Nature Chemistry*, **2012**, 4, 443–455
- [37] D. Xiang, X. Wang, C. Jia, T. Lee, X. Guo, *Chemical Review*, **2016**, 116, 4318–4440
- [38] H. Sellers, A. Ulman, Y. Shnidman, J. E. Eilers, *Journal of the American Chemical Society*, **1993**, 115, 9389–9401.
- [39] K. M. Beardmore, J. D. Kress, N. Gronbeck-Jensen, A. R. Bishop, *Chemical Physics Letters*, **1998**, 286, 40–45.
- [40] Y. Yourdshahyan, H. K. Zhang, A. M. Rappe, *Physical Review B*, **2001**, 63, (081405)1–4
- [41] K. Szelagowska-Kunstman, P. Cyganik, B. Schüpbach, A. Terfort, *Physical Chemistry Chemical Physics*, **2010**, 12, 4400–4406.
- [42] D. Kafer, A. Bashir, G. Witte, *The Journal of Physical Chemistry C*, **2007**, 111, 10546–10551

- [43] L. Patrone, S. Palacin, J. Charlier, F. Armand, J. P. Bourgoin, H. Tang, S. Gauthier, *Physical Review Letters* **2003**, 91, (096802)1-4
- [44] J. D. Monnell, J. J. Stapleton, S. M. Dirk, W. A. Reinert, J. M. Tour, D. L. Allara, P. Weiss, *Phys. Chem. B* **2005**, 109, 20343-20349
- [45] F. K. Huang, R. C. Horton, D. C. Myles, R. L. Garrell, *Langmuir*, **1998**, 14, 4802-4808
- [46] Y. Sato, F. Mizutania, *Physical Chemistry Chemical Physics*, **2004**, 6, 1328-1331.
- [47] K. Yokota, M. Taniguchi, T. Kawai, *Journal of the American Chemical Society*, **2007**, 129, 5818-5819
- [48] H. T. Rong, S. Frey, Y. J. Yang, M. Zharnikov, M. Buck, M. Wohn, C. Woll, G. Helmchen, *Langmuir*, **2001**, 17, 1582-1593.
- [49] P. Cyganik, K. Szelagowska-Kunstman, A. Terfort, M. Zharnikov, *The Journal of Physical Chemistry C*, **2008**, 112, 15466– 15473.
- [50] P. Cyganik, M. Buck, J. D. Wilton-Ely, C. Wöll, *The Journal of Physical Chemistry B*, **2005**, 109, 10902-10908
- [51] K. Heister, H. T. Rong, M. Buck, M. Zharnikov, M. Grunze, L. S. O. Johansson, *The Journal of Physical Chemistry B*, **2001**, 105, 6888-6898.
- [52] A. Shaporenko, J. Müller, T. Weidner, A. Terfort, M. Zharnikov, *Journal of the American Chemical Society*, **2007**, 129, 2232-2233
- [53] J. Cyriac, T. Pradeep, H. Kang, R. Souda, R. G. Cooks, *Chemical Review*, **2012**, 112, 5356–5411.
- [54] M. Senoner, W. E. S. Unger, *Journal of Analytical Atomic Spectrometry*, **2012**, 27, 1050–1068.
- [55] J. C. Vickerman, *Analyst*, **2011**, 136, 2199– 2217.
- [56] A. M. Belu, D. J. Graham, D. G. Castner, *Biomaterials*, **2003**, 24, 3635–3653.
- [57] M. Pacholski, N. Winograd, *Chemical Review*, **1999**, 99, 2977–3005.
- [58] A. Benninghoven, *Angewandte Chemie International Edition*, **1994**, 33, 1023–1043.
- [59] D. Rading, R. Kersting, A. Benninghoven, *Journal of Vacuum Science & Technology A*, **1999**, 18, 312-319
- [60] M. Dendzik, A. Terfort, P. Cyganik, *The Journal of Physical Chemistry C*, **2012**, 116, 19535– 19542.
- [61] S. C. Wong, N. P. Lockyer, J. C. Vickerman, *Surface and Interface Analysis*, **2005**, 37, 721-730
- [62] C. L. McGuinness, A. Shaporenko, M. Zharnikov, A. Walker, D. L. Allara, *The Journal of Physical Chemistry C*, **2007**, 111, 4226-4234
- [63] H. Y. Nie, *Analytical Chemistry*, **2010**, 82, 3371-3376
- [64] E. Cooper, G. Leggett, *Langmuir*, **1998**, 14, 4795-4801
- [65] Z. Shi, P. Lu, A. Walker, *Langmuir*, **2012**, 28, 16909-16916
- [66] Z. Zhu, D. L. Allara, N. Winograd, *Applied Surface Science*, **2006**, 19, 6686-6688
- [67] L. M. Rodríguez, L. J. Cristina, L. S. Alarcón, B. Blum, R. C. Salvarezza, L. Xi, W. M. Lau, E. A. Sánchez, J. E. Gayone, O. Grizzi, *Nuclear Instruments and Methods in Physics Research B*, **2001**, 269, 924–931
- [68] M. Zharnikov, S. Frey, H. T. Rong, Y. J. Yang, K. Heister, M. Buck, M. Grunze, *Physical Chemistry Chemical Physics*, **2000**, 2, 3359–3362.
- [69] T. Weidner, A. Shaporenko, J. Müller, T. Schmid, P. Cyganik, A. Terfort, M. Zharnikov, *The Journal of Physical Chemistry C*, **2008**, 112, 12495-12506
- [70] W. Azzam, P. Cyganik, G. Witte, M. Buck, C. Wöll, *Langmuir*, **2003**, 19, 8262–8270.
- [71] Cyganik, M. Buck, W. Azzam, C. Wöll, *The Journal of Physical Chemistry B*, **2004**, 108, 4989–4969.
- [72] Encyklopedia fizyki; Państwowe Wydawnictwo Naukowe; Warszawa 1974
- [73] M. Baghbanzadeh, F. C. Simeone, C. M. Bowers, K. C. Liao, M. Thuo, M. S. Miller, T. B. Carmichael, G. M. Whitesides, *Journal of the American Chemical Society*, **2014**, 136, 16919– 16925.
- [74] K. Forster-Tonigold A. Gross, *Surface Science*, **2015**, 640, 18–24
- [75] P. A. Redhead, *Vacuum*, **1962**, 12, 203–211.

7. Dodatkowe osiągnięcia

Publikacje naukowe autora, które nie weszły w skład niniejszej pracy doktorskiej:

1. Anna Krzykawska, Jakub Ossowski, Tomasz Żaba, Piotr Cyganik „*Binding group for Highly Ordered SAMs Formation: Carboxylic versus Thiols*” Chemical Communications, **2017**, 53, 5748-5751
2. Anna Krzykawska, Monika Szwed, Jakub Ossowski, Piotr Cyganik „*Odd-Even Effect in Molecular Packing of Self-Assembled Monolayers of Biphenyl-Substituted Fatty Acid on Ag(111)*” The Journal of Physical Chemistry C, **2018**, 122, 919-928

Nagrody i stypendia:

Nazwa	Rok	Instytucja finansująca
Stypendium dla zagranicznych studentów “Dorothy M. and Earl S. Hoffman Travel Grant”	2012 2013 2014	American Vacuum Society
Stypendium Rektora Uniwersytetu Jagiellońskiego dla najlepszych doktorantów	2015/2016	Uniwersytet Jagielloński
Specjalne stypendium im. Mariana Smoluchowskiego dla doktorantów Krakowskiego Konsorcjum Naukowego im. Mariana Smoluchowskiego „Materia-Energia-Przyszłość”	2015/2016	85% Europejski Fundusz Społeczny 15% Środki krajowe
Stypendium START dla najzdolniejszych młodych polskich naukowców do 30 roku życia	2017/2018	Fundacja na rzecz Nauki Polskiej
Stypendium doktorskie ETIUDA 5	2017/2018	Narodowe Centrum Nauki

Ustne wystąpienia na konferencjach międzynarodowych:

Rok	Nazwa konferencji	Miejsce	Tytuł wystąpienia
2012	AVS 59 th International Symposium & Exhibition	Tampa, FL, Stany Zjednoczone	<i>SIMS as a Method for Probing Stability of the Molecule-Substrate Interface in SAMs</i>
2013	AVS 60 th International Symposium & Exhibition	Long Beach, CA, Stany Zjednoczone	<i>Relative Stability of Thiols and Selenols SAMs on Ag(111) – Exchange and Desorption Experiments</i>
2014	AVS 61 st International Symposium & Exhibition	Baltimore, MD, Stany Zjednoczone	<i>Relative Stability of S-Au and Se-Au Bonding in Aromatic and Aliphatic Self-Assembled Monolayers – Exchange and Ion Desorption Experiments</i>
2015	12 th International Conference on Nanosciences and Nanotechnologies	Saloniki, Grecja	<i>Relative Stability of S-Au and Se-Au Bonding in Aromatic and Aliphatic Self-Assembled Monolayers – Exchange and Ion Desorption Experiments</i>
2016	XX SIMS Europe	Munster, Niemcy	<i>Oscillations in stability of consecutive chemical bonds at the molecule-metal interface in Self-Assembled Monolayers revealed by static SIMS.</i>
	16 th International Conference on Organized Molecular Films	Helsinki, Finlandia	<i>Oscillations in stability of consecutive chemical bonds at the molecule-metal interface in Self-Assembled Monolayers revealed by static SIMS.</i>
2017	21 st International Conference on Secondary Ion Mass Spectrometry	Kraków, Polska	<i>Thiolate versus Selenolate: Molecule-Substrate Interface Analysis in Aromatic Self-Assembled Monolayers by S-SIMS and TP-SIMS</i>
2018	17 th International Conference on Organized Molecular Films	Brooklyn, NY, Stany Zjednoczone	<i>Oscillations in stability of consecutive chemical bonds at the molecule-metal interface</i>

Oscillations in the Stability of Consecutive Chemical Bonds Revealed by Ion-Induced Desorption**

Jakub Ossowski, Jakub Rysz, Mariusz Krawiec, Dawid Maciazek, Zbigniew Postawa, Andreas Terfort, and Piotr Cyganik*

Abstract: While it is a common concept in chemistry that strengthening of one bond results in weakening of the adjacent ones, no results have been published on if and how this effect protrudes further into the molecular backbone. By binding molecules to a surface in the form of a self-assembled monolayer, the strength of a primary bond can be selectively altered. Herein, we report that by using secondary-ion mass spectrometry, we are able to detect for the first time positional oscillations in the stability of consecutive bonds along the adsorbed molecule, with the amplitudes diminishing with increasing distance from the molecule–metal interface. To explain these observations, we have performed molecular dynamics simulations and DFT calculations. These show that the oscillation effects in chemical-bond stability have a very general nature and break the translational symmetry in molecules.

Self-assembled monolayers (SAMs)^[1] are a nanotechnological system, in which molecules are chemically bonded to a substrate in an ordered and oriented fashion. The influence of the strength of the molecule–substrate bond on the structure and stability of SAMs is still poorly understood even for the most simple system of methanethiol on Au(111).^[2] As it is known from other fields of chemistry, the formation of a strong bond (in this case to the surface) should lead to a weakening of the adjacent bonds within the molecules. Thus, it would be interesting from a very basic point of view as well as technologically relevant to determine these influences.

We decided to take a new approach by exploiting static secondary-ion mass spectrometry (SSIMS) in combination

with the molecular dynamics (MD) simulation of such experiments and density functional theory (DFT) calculations. As model SAMs we have selected two homologous series of the general form $\text{CH}_3-(\text{C}_6\text{H}_4)_2-(\text{CH}_2)_n-\text{S}(\text{Se})/\text{Au}(111)$, (BPnS(Se), $n=1-6$), for which either sulfur atoms or selenium atoms (BPnSe) act as a binding groups to the Au(111) substrate. Previous microscopic^[3-5] and spectroscopic^[6-9] studies demonstrated that the BPnS(Se)/Au(111) packing structure, unlike other SAMs, remains virtually the same for the S and Se analogues within both series. This means that intermolecular interactions in these SAMs are identical when comparing the respective members of both families and thus the only source of difference in stability between them is the binding atom (S vs. Se). Analysis of such SAMs gives a direct way to trace molecule–substrate interface energetics.

Positive and negative SSIMS mass spectra are presented in Figure S1 in the Supporting Information. The most interesting information is found in the positive mass spectra where a significant emission of secondary ions related to the complete molecule $M_{\text{S/Se}}^+$ and its desulfurized ($[M-\text{S}]^+$) or deselenized ($[M-\text{Se}]^+$) fragments, respectively, is observed. Interestingly, the M_{S}^+ emission is much higher than the M_{Se}^+ , while the emission of $[M-\text{S}]^+$ is much lower than the that of $[M-\text{Se}]^+$ (see Figure S2). Since emission of an $M_{\text{S/Se}}^+$ ion requires Au–S(Se) bond scission, we can correlate a stronger M_{S}^+ signal with a lower stability of the Au–S bond compared to the Au–Se bond, in line with previous exchange experiments.^[10] Following this argumentation, we can correlate the reduced emission of $[M-\text{S}]^+$ compared to $[M-\text{Se}]^+$ with a higher stability of the S–C bond than the Se–C bond in these SAMs. Such behavior could be explained considering that the valence electrons of the S (or Se) atom are involved in bonding with the Au substrate atom and with its neighboring C atom. The increased involvement of valence electrons of the S(Se) atom in one of these chemical bonds should result in lower involvement of these electrons in the second bond, consequently reducing the stability of the second bond. We may ask if modifying the strength of the bond to the substrate by an S→Se substitution will influence additional chemical bonds in its vicinity. To answer this question, we have calculated the intensity ratio of the signals of identical ions ejected from BPnS/Au(111) and BPnSe/Au(111) SAMs ($n=2-4$). These ions were generated by the scission of one of four consecutive chemical bonds along the molecular chain, starting from the headgroup atom (Figure 1 a). The resulting data (Figures 1 b–d) show a very clear positional oscillation which decreases with increasing distance from the metal–molecule interface. Following previous argumentation the substitution of the S atom by the more strongly bound Se

[*] J. Ossowski, Dr. J. Rysz, D. Maciazek, Prof. Z. Postawa, Dr. P. Cyganik

Smoluchowski Institute of Physics

Jagiellonian University

Reymonta 4, 30059 Kraków (Poland)

E-mail: piotr.cyganik@uj.edu.pl

Dr. M. Krawiec

Institute of Physics, Marie Curie Skłodowska University, Pl M. Curie Skłodowskiej 1, 20-031 Lublin (Poland)

Prof. A. Terfort

Institute of Inorganic and Analytical Chemistry, Goethe University Max-von-Laue Strasse 7, 60438 Frankfurt (Germany)

[**] This work was financially supported by National Science Centre Poland (grant 2011/01/B/ST4/00665). The SSIMS equipment was purchased thanks to the European Regional Development Fund (grant POIG.02.02.00-12-023/08).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201406053>.

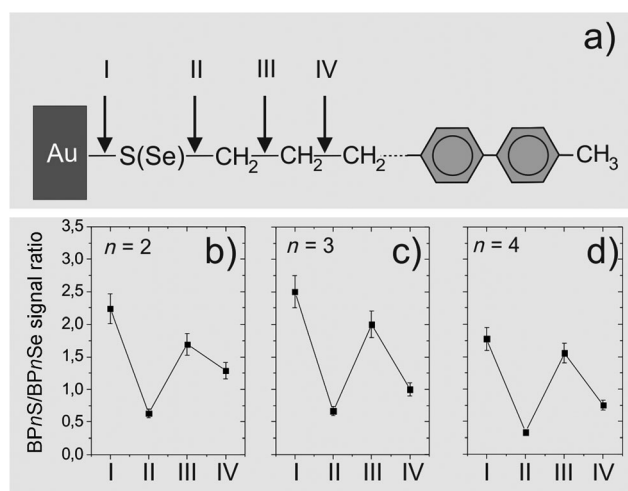


Figure 1. SSIMS data analysis. a) the location of the four probed, consecutive chemical bonds. Emission of M^+ , $[M-S(Se)]^+$, $[M-CH_2S(Se)]^+$, and $[M-CH_2CH_2S(Se)]^+$ secondary ions corresponds to scission of bond I, II, III, and IV, respectively. b–d) the relative intensities of the positive ions emitted from BPnS/Au(111) and BPnSe/Au(111) SAMs (for $n=2$ (b), $n=3$ (c) and $n=4$ (d)) corresponding to the scission of indicated bonds.

atom leads to a shift of valence electrons from the neighboring Se–C¹ bond towards the Au–Se bond reducing the stability of the Se–C¹ bond. The decrease in the Se–C¹ bond stability results, in turn, in a shift of the valence electrons of the C¹ atom towards the C² atom leading to an increased strength of the C¹–C² bond, and so on. As a consequence, we propose that: 1) increase of stability of the headgroup atom bonding to the substrate by changing from S→Se induces a chain of alternating modifications of the stability of the neighboring chemical bonds in the molecule, and 2) the disturbances introduced into electronic structure of the aliphatic chain by chemical bonding to the substrate by the headgroup atom diminish at larger distances from the molecule–substrate interface because the dislocation of the valence electrons becomes less and less.

Our analysis indicates an alternating change of the bond stability on comparison of the respective data from the thiol and selenol series. We may ask if a similar effect can be observed within each of these homologous series separately and how these changes are related to each other? As shown in Figure 2a–c a significant odd–even variation (with respect to the number n within each series) exists for the emission of $[C_{15}H_{15}]^+$, $[C_{14}H_{13}]^+$, and $[C_{16}H_{17}]^+$ fragments from the BPnS(Se)/Au(111) SAMs. To desorb for instance a $[C_{15}H_{15}]^+$ fragment from BPnS(Se)/Au(111) SAMs with an increasing number n along the homologous series, consecutive chemical bonds have to be cleaved (Figure 2a). Thus, for $n=1$ the S(Se)–C¹ bond has to be cleaved, for $n=2$ the C¹–C² bond, and so on. The data shown in Figure 2a deliver several crucial pieces of information. First, considering our proposition that the relative signal of identical ions ejected from BPnS/Au(111) and BPnSe/Au(111) SAMs is proportional to the strength of the bond that needs to be broken, the odd–even oscillation in Figure 2a indicates alternating changes in the

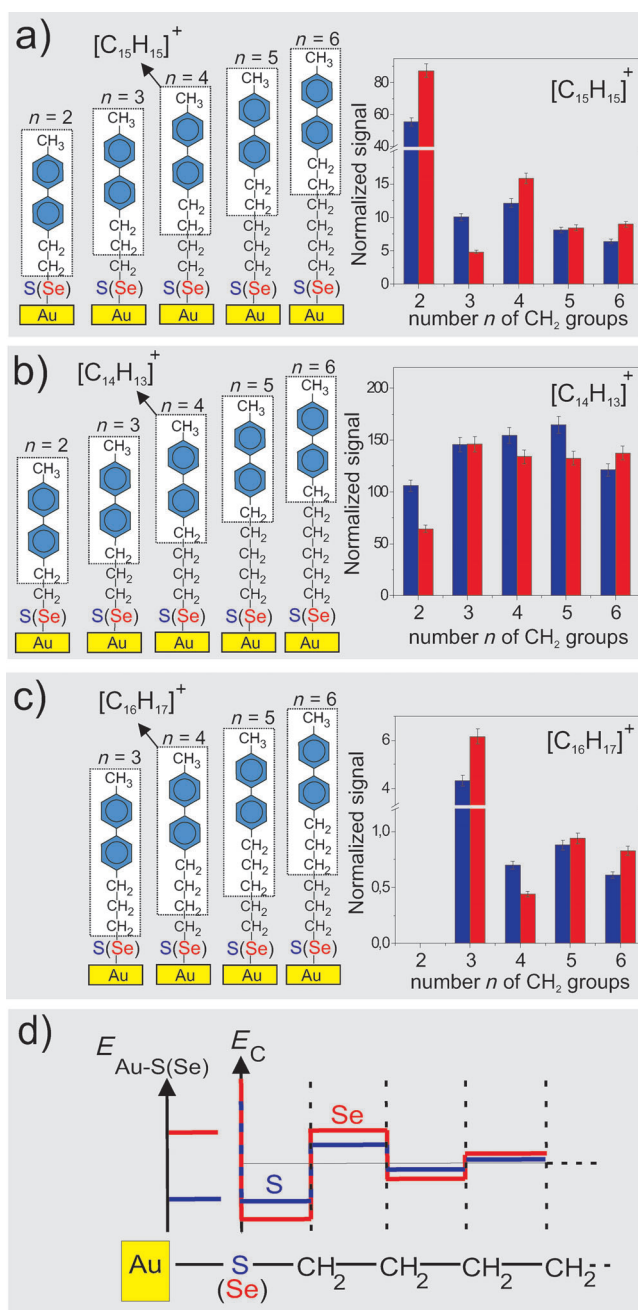


Figure 2. SSIMS data analysis. a) the normalized signal of the $[C_{15}H_{15}]^+$ emission for BPnS/Au(111) (blue bars) and BPnSe/Au(111) (red bars). b) the respective data for the $[C_{14}H_{13}]^+$ emission and c) for the $[C_{16}H_{17}]^+$ emission. The white boxes in the schemes on the left side of panels (a)–(c) show which part of the individual molecules corresponds to the given type of secondary ion, also indicating the location of the scission resulting in its emission. Note that the phase of this odd–even effect depends on the length of the analyzed fragment and, therefore, this odd–even effect is not a consequence of the established odd–even^[2,3] variation in the film density of these SAMs. d) Summary of the SSIMS results: i) The higher bond energy of Se–Au than S–Au and ii) the resulting oscillations in the bond energies of the consecutive bonds along the molecular backbone. The effect diminishes with increasing distance from the molecule–substrate interface, but generally shows a higher amplitude for the selenium-based SAMs.

stability of consecutive chemical bonds along the molecule in the direction away from the molecule–substrate interface towards the biphenyl group. Second, this bond-stability oscillation effect has the same phase for BPnS/Au(111) and BPnSe/Au(111) SAMs with, however, much higher modulation amplitude for the Se system. Third, the amplitude of these oscillations quickly diminishes with increasing distance from the molecule–substrate interface. All these observations are fully consistent with the data shown in Figure 1. Following our simple qualitative explanation, more pronounced oscillations are expected for BPnSe/Au(111) as compared to BPnS/Au(111) SAMs owing to a stronger bonding of the Se system to the Au(111) substrate. These conclusions are supported by analogous data shown in Figure 2b, where the strong signal of the $[C_{14}H_{13}]^+$ fragment is analyzed. This fragment is shorter by one CH_2 group than the $[C_{15}H_{15}]^+$ fragment therefore we need to shift our analysis by one chemical bond away from the molecule–substrate interface. As a result, the amplitude of the oscillations is reduced because of the greater distance from the molecule–substrate interface and, more importantly, the phase of the odd–even effect is reversed. A similar trend is also present in the somewhat weaker signal of the $[C_{16}H_{17}]^+$ fragment which can only be emitted for $n = 3–6$. In this case, we need to shift the analysis by one chemical bond in the direction of the molecule–substrate interface as compared to the analysis for the $[C_{15}H_{15}]^+$ fragment. As expected, data shown in Figure 2c fully confirm such a scenario for both BPnS/Au(111) and BPnSe/Au(111) SAMs: a stronger odd–even effect and a reversal of the phase can be observed. Again, the magnitude of the odd–even oscillation is higher for the BPnSe/Au(111) SAMs and diminishes in both cases with increasing number n . Note that the phase of this odd–even effect depends on the length of the analyzed fragment and, therefore, this odd–even effect is *not* a consequence of the known odd–even^[2,3] variation in the film density of these SAMs.

We believe that the above SSIMS measurements reveal for the first time the oscillation of bond stability along the molecule backbone as shown schematically in Figure 2d. It is worth mentioning that such a modulation of bond energy cannot only be attained by changing the anchoring atom ($S \rightarrow Se$), but also the substrate ($Au \rightarrow Ag$), which results in very similar observations (data will be published elsewhere). However, in all cases our hypothesis postulates that the emission efficiency of a given molecular secondary ion is correlated with the stability of the respective chemical bond that has to be cleaved to enable emission of this ion. The justification of such a correlation is discussed in detail in the Supporting Information. In short, two issues must be considered: the desorption and the ionization mechanism. Two distinct desorption mechanisms leading to the emission of neutral molecular fragments were identified by previous studies on collision-cascade and chemical-reaction based processes.^[11–14] Whereas the chemical reaction mechanism quite naturally explains the high sensitivity of emission towards the stability of the respective cleaved bond, such sensitivity for the energetic collision-cascade based emission is not obvious. To address this issue we have performed simulations of BP3S/Au(111) sputtering induced by 8 keV Bi

atoms using MD simulations. To probe possible influences of the Au–S and S–C bond stability on the efficiency of the sputtering process, two sets of MD simulations have been performed (Figures 3 and S3). The first set of calculations was performed on a BP3S/Au(111) system having non-modified Au–S and S–C bond strength, while the second set of simulations was performed on a system, where the Au–S bond strength was increased by 10% and the S–C bond strength was reduced by 10%. The data presented in Figure 3

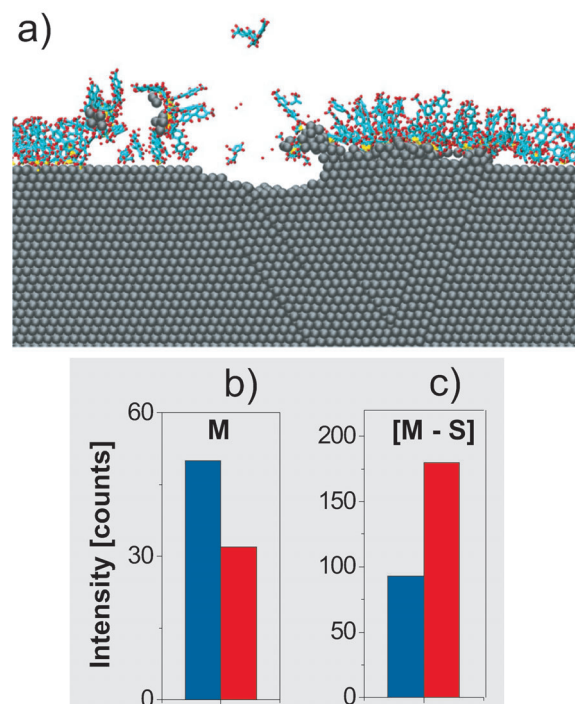


Figure 3. Analysis of MD simulations for the sputtering of BP3S/Au(111) SAMs with 8 keV Bi projectiles. a) the impact of a single Bi^+ projectile on a BP3S/Au(111) SAM. b),c) the emission of the complete molecule (M) and desulfurized fragment (M–S) resulting from a compilation of 1100 impact events: blue bars correspond to the emission from native BP3S/Au(111) system and red bars corresponds to a modified BP3S/Au(111) system, in which the Au–S bond strength was increased by 10% and the S–C bond strength was decreased by 10%. Full mass spectra calculated for both systems are shown in Figure S3.

show that even such a small modification of bond strengths results in a 40% reduction in $[M]^+$ emission (scission of the Au–S bond) and an almost 100% increased emission of $[M-S]^+$ fragments (scission of the S–C bond). These results are consistent with our SSIMS data in Figure S2 and confirm that small changes in the stability of the chemical bonds can strongly affect the collision-cascade based emission. We can, therefore, conclude that both, desorption of molecular fragments by ion-induced chemical reactions or by simple collision-cascade mechanisms, are correlated with the stability of the respective bonds, which become cleaved during the desorption process. But can this trend be altered by the ionization process? As detailed in the Supporting Information, this presumably is not the case. Generally, experiments

analyzing emission of neutral fragments^[13,14] and the DFT calculations for these SAMs^[15] with the possible ionization process by electron transfer^[16] or by excited precursor fragmentation^[16] show that the ionization process does not influence significantly the correlation between desorption process and stability of a cleaved chemical bond.

To understand if an alternating strengthening and weakening of several consecutive bonds can in fact be the result of a change at a terminal bond, we have performed DFT calculations. First, binding energies of chemical bonds within an individual BP3S molecule adsorbed on the Au(111) surface were analyzed. The results are shown in Figure 4a exhibiting

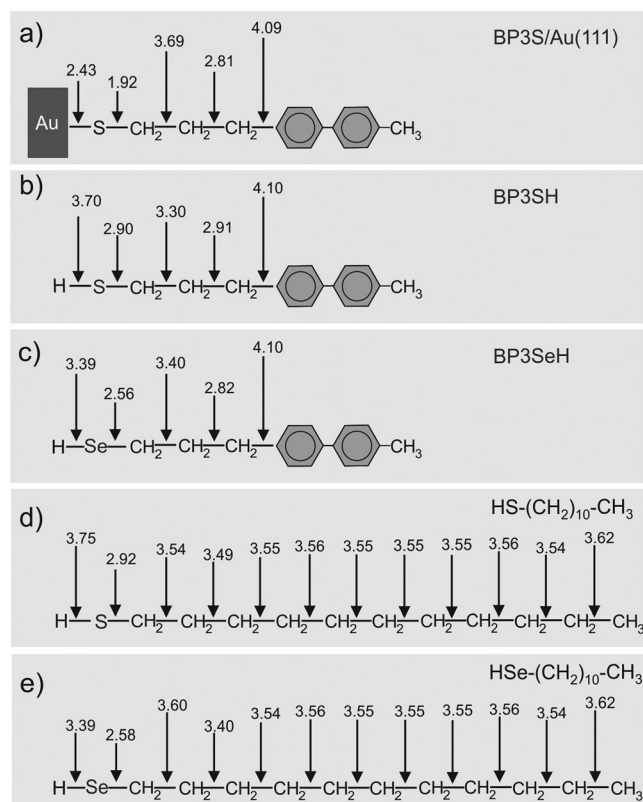


Figure 4. Summary of the DFT calculation results for individual bond energies (in eV) for a) the BP3S/Au(111) monolayer, b) free BP3SH molecule, c) free BP3SeH molecule, d) free HS-(CH₂)₁₀-CH₃ molecule, and e) free HSe-(CH₂)₁₀-CH₃ molecule.

clear oscillation in the binding energy of consecutive chemical bonds. Comparing the phase of the observed oscillations with the SSIMS experiments shown in Figure 2, we conclude that a higher emission of a given secondary ion is indeed correlated with a lower binding energy of the respective chemical bond that has to be cleaved. As a next step, calculations for unbound BP3SH and BP3SeH molecules were performed (Figure 4b,c) exhibiting an oscillation in the binding energy of consecutive bonds with the same phase as for the Au(111) surface bonded molecule. Moreover the amplitude of these oscillations is clearly higher for the Se based molecule. To separate the influence of the biphenyl group on the observed oscillations, the bond strengths in long

alkanethiol and alkaneselenol molecules were calculated (Figure 4d,e). These data show a quickly diminishing oscillation in binding energies with increasing distance from the SH/SeH terminus, again with higher amplitude for the SeH case. Altogether, these calculations clearly indicate that the observed effect of the bond stability oscillation is not exclusively related to the molecule–substrate interface but has a much more general character in chemistry. In this case, the substitution of a methylene group (C–C bond energy 3.55 eV) by a sulfur or selenium atom (C–S and C–Se bond energy 2.92 and 2.58 eV, respectively) results in breaking the translational symmetry in the aliphatic chain by modifying the energy of the next three consecutive C–C bonds with a decreasing oscillating strength, finally recovering the ‘normal’ value of 3.55 eV. For BP3SH molecules this effect is significantly amplified since the other end of the short aliphatic chain is attached to a biphenyl group with a much stronger C³–C⁴ bond (4.1 eV) which itself causes similar oscillations amplifying this effect in comparison to long alkanethiols.

In conclusion, our experiments and calculations show that by using the SSIMS technique we can not only trace the changes in the binding stability of SAMs, but, more importantly, analyze subtle variations in the molecule’s internal energetics. With this approach, we could find positional oscillations in bond energy, that are not only related to the molecule–substrate interface, but have a general character in chemistry related to breaking translational symmetry in molecules. Although chemically quite intuitive, it is very surprising that this effect has neither been described nor considered before in the literature. It is reasonable to assume that these effects became blurred in the more traditional techniques, such as thermal or electrochemical desorption, owing to the comparably slow ramping of the global energies (temperature or potential, respectively). This slow ramping permits a reconstruction of molecule–substrate interface which affects the bond-cleavage processes. To detect the effect of the binding energies directly, the exploitation of the pico-second time scale of the desorption processes within the SSIMS technique was essential.

Received: June 9, 2014

Revised: August 14, 2014

Published online: December 4, 2014

Keywords: chemical bonding · density functional calculations · mass spectrometry · molecular dynamics · self-assembled monolayers

- [1] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103.
- [2] H. Häkkinen, *Nat. Chem.* **2012**, *4*, 443.
- [3] W. Azzam, P. Cyganik, G. Witte, M. Buck, C. Wöll, *Langmuir* **2003**, *19*, 8262.
- [4] P. Cyganik, M. Buck, W. Azzam, C. Wöll, *J. Phys. Chem. B* **2004**, *108*, 4989.
- [5] P. Cyganik, K. Szelagowska-Kunstman, A. Terfort, M. Zharnikov, *J. Phys. Chem. C* **2008**, *112*, 15466.

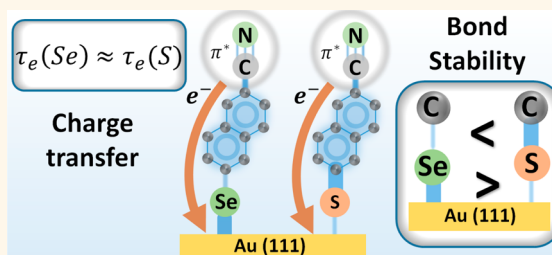
- [6] H. T. Rong, S. Frey, Y. J. Yang, M. Zharnikov, M. Buck, M. Wühn, C. Wöll, G. Helmchen, *Langmuir* **2001**, *17*, 1582.
- [7] K. Heister, H. T. Rong, M. Buck, M. Zharnikov, M. Grunze, L. S. O. Johansson, *J. Phys. Chem. B* **2001**, *105*, 6888.
- [8] A. Shaporenko, J. Müller, T. Weidner, A. Terfort, M. Zharnikov, *J. Am. Chem. Soc.* **2007**, *129*, 2232.
- [9] T. Weidner, A. Shaporenko, J. Müller, T. Schmid, P. Cyganik, A. Terfort, M. Zharnikov, *J. Phys. Chem. C* **2008**, *112*, 12495.
- [10] K. Szelańska-Kunstman, P. Cyganik, B. Schüpbach, A. Terfort, *Phys. Chem. Chem. Phys.* **2010**, *12*, 4400.
- [11] D. E. Riederer, R. Chatterjee, S. W. Rosencrance, Z. Postawa, T. D. Dunbar, D. L. Allara, N. Winograd, *J. Am. Chem. Soc.* **1997**, *119*, 8089.
- [12] F. Vervaecke, S. Wyczawska, P. Cyganik, Z. Postawa, M. Buck, R. E. Silverans, P. Lievens, E. Vandeweert, *J. Phys. Chem. C* **2008**, *112*, 2248.
- [13] F. Vervaecke, S. Wyczawska, P. Cyganik, J. Bastiaansen, Z. Postawa, R. E. Silverans, E. Vandeweert, P. Lievens, *ChemPhys-Chem* **2011**, *12*, 140.
- [14] S. Wyczawska, P. Cyganik, A. Terfort, P. Lievens, *ChemPhys-Chem* **2011**, *12*, 2554.
- [15] G. Heimel, L. Romaner, J. Bredas, E. Zojer, *Langmuir* **2008**, *24*, 474.
- [16] J. C. Vickerman, D. Briggs, *TOF-SIMS: Surface Analysis by Mass Spectrometry*, IM Publications, **2001**.

Thiolate *versus* Selenolate: Structure, Stability, and Charge Transfer Properties

Jakub Ossowski,[†] Tobias Wächter,[‡] Laura Silies,[§] Martin Kind,[§] Agnieszka Noworolska,[†] Florian Blobner,^{||} Dominika Gnatek,[†] Jakub Rysz,[†] Michael Bolte,[§] Peter Feulner,^{||} Andreas Terfort,^{*,§} Piotr Cyganik,^{*,†} and Michael Zharnikov^{*,‡}

[†]Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Krakow, Poland, [‡]Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany, [§]Institut für Anorganische und Analytische Chemie, Universität Frankfurt, Max-von-Laue-Straße 7, 60438 Frankfurt, Germany, and ^{||}Physikdepartment E20, Technische Universität München, 85747 Garching, Germany

ABSTRACT Selenolate is considered as an alternative to thiolate to serve as a headgroup mediating the formation of self-assembled monolayers (SAMs) on coinage metal substrates. There are, however, ongoing vivid discussions regarding the advantages and disadvantages of these anchor groups, regarding, in particular, the energetics of the headgroup–substrate interface and their efficiency in terms of charge transport/transfer. Here we introduce a well-defined model system of 6-cyanonaphthalene-2-thiolate and -selenolate SAMs on Au(111) to resolve these controversies. The exact structural arrangements in both types of SAMs are somewhat different, suggesting a better SAM-building ability in the case of selenolates. At the same time, both types of SAMs have similar packing densities and molecular orientations. This permitted reliable competitive exchange and ion-beam-induced desorption experiments which provided unequivocal evidence for a stronger bonding of selenolates to the substrate as compared to the thioliates. Regardless of this difference, the dynamic charge transfer properties of the thiolate- and selenolate-based adsorbates were found to be nearly identical, as determined by the core–hole–clock approach, which is explained by a redistribution of electron density along the molecular framework, compensating the difference in the substrate–headgroup bond strength.



KEYWORDS: selenolate · self-assembly · self-assembled monolayers · charge transfer · bond strength · metal surfaces

Self-assembled monolayers (SAMs) are an indispensable playground of surface science and physical chemistry of interfaces as well as an important element of modern nanotechnology.^{1–3} Numerous applications of these systems rely on the flexible molecular design of their constituents involving, in its turn, a suitable combination of characteristic building blocks, such as a tail group, molecular backbone, and headgroup. Among different kinds of SAMs, monolayers of thiols and disulfides on coinage metal substrates are probably the most frequently used ones because of their robustness, ease of preparation, and reasonable stability.^{3,4} The thiolate headgroup emerging upon adsorption of thiols and disulfides provides sufficiently strong but flexible anchoring to the substrate, enabling efficient lateral diffusion of the adsorbed molecules to form highly ordered 2D assemblies. A noticeably stronger, covalent-like binding can result in the inhibition of

the lateral mobility and poor structural perfection as it, for example, happens in siloxane-based SAMs on SiO_x, whereas a weaker anchoring is associated with a limited stability.⁵

Along with the strength of the headgroup–substrate bond, the corrugation of the binding energy surface for the given headgroup/substrate combination, that is, a two-dimensional energetic landscape of the substrate seen by the headgroups, is of importance.¹ In case of a strong corrugation, as occurs for thiolate-based SAMs on Au(111),^{1,4,6–8} the molecular lattice becomes pinned to the structural template provided by the substrate, which can result in reduced packing density^{1,4,6–8} and/or in limited structural perfection^{9–13} if the optimal molecular arrangement does not fit the substrate structure. In contrast, a weak corrugation of the binding energy surface allows formation of optimal molecular lattices, mediated, to a significant extent, by the

* Address correspondence to michael.zharnikov@urz.uni-heidelberg.de, piotr.cyganik@uj.edu.pl, aterfort@chemie.uni-frankfurt.de.

Received for review February 17, 2015 and accepted April 10, 2015.

Published online April 10, 2015
10.1021/acs.nano.5b01109

© 2015 American Chemical Society

backbone–backbone interactions as this happens in alkanethiolate SAMs on Ag(111).^{1,4,14,15} A further parameter associated with a particular headgroup–substrate combination is the bending potential which enters the balance of structural forces, affecting the packing density and molecular orientation.^{16–19}

Apart from the structural effects, charge transport properties of molecular anchors are important because they define the electronic coupling of the SAM constituents to the (conductive) substrate. A good coupling is favorable for applications in molecular and organic electronics.^{20,21} In the former case, this guarantees an efficient and rapid charge transfer between the functional molecule and the bottom electrode. In the latter case, this improves the conductivity of the buffer SAM film, improving the overall device performance. In addition, the docking chemistry at the substrate side of the SAM affects the level alignment at the metal–organic interface.²²

In view of the above aspects, optimization of the headgroup seems to be a promising way to tune the structural and electronic properties of SAMs. Among other options, the use of elements with the same valence electron configurations as sulfur, such as its homologues in the 16th group of the periodic table, seems to be a reasonable choice for SAMs on coinage metal substrates. Accordingly, the suitable candidates are selenium and tellurium, with a clear preference for the former element in view of the limited stability of tellurium-based monolayers.²³ Along these lines, a variety of aliphatic and aromatic SAMs with the selenol headgroup have been prepared on Au(111) and Ag(111) substrates and studied to different extents.^{19,24–45} The quality of these SAMs was in most cases comparable or even superior to that of the monolayers prepared from the thiol analogues. The latter was particularly the case for the aromatic SAMs on Au(111), including those with the phenyl, biphenyl, and anthracene backbone.^{35,37,40–42,44} For these monolayers, a significant improvement of the quality in terms of the structural perfection, domain size, and long-range order was observed. This was explained by the ability of the selenolates to adjust the surface lattice of the substrate to the most favorable 2D arrangement of the SAM-building molecules^{35,40,44} or, alternatively, by a smaller corrugation of the binding energy surface for selenolates on Au(111) as compared to that for thiols.^{37,41,40,44}

In spite of the general agreement regarding the quality improvement upon the use of selenium instead of sulfur as the headgroup, there is still a controversy regarding the strength of the headgroup–substrate bond for the thiol-based and selenol-based SAMs on Au(111). The selenium–gold bond was considered as both stronger^{25,27,28,35,46} and weaker^{24,37} than the sulfur–gold one. These controversial conclusions were derived on the basis of different experiments, using different test systems which were characterized to a

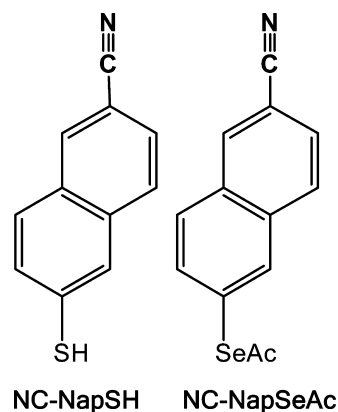


Figure 1. Molecules used in this study along with their acronyms. During the formation of the monolayers, the proton and the acetyl group, respectively, become cleaved off, so that the adsorbed molecules can be assigned as NC-NapS and NC-NapSe.

limited extent only or/and were not equivalent. In particular, the conclusion regarding the comparably weaker selenium–gold bond was based on the results of thermal desorption spectroscopy experiments on benzenethiolate and benzeneselenolate SAMs which have rather different packing densities and quality.³⁷ A further controversial point is the conductance of the selenium–gold bond. According to some reports, thiolate-based molecules have a lower barrier to tunneling and therefore a higher conductance than their selenolate-based analogues.⁴⁷ At the same time, according to other reports, the electronic conductance of selenium-based aromatic molecules is comparable to that of their sulfur analogues.²² Finally, there are several studies which claim that the charge injection barrier is lower for the gold–selenium bond than for the gold–sulfur bond,⁴⁸ and the electronic conductance of selenium-based molecules is significantly higher than that of their sulfur analogues.^{49–51} The above discrepancies can be related to differences in the test systems used for the respective experimental studies and theoretical simulations (*e.g.*, aliphatic⁴⁷ or aromatic^{49,50} ones) but also to certain limitations of the standard experimental approaches used to measure conductance in molecular assemblies. These limitations include an uncertainty regarding the number of molecules involved in the charge transport and quality of the top contact, that is, the electrical contact to the tail group of the molecules (the bottom contact is mediated by the headgroup and provided usually by the metal substrate).

In the present work, we try to clarify the above-mentioned controversies using model systems based on 6-cyanonaphthalene-2-thiolate and -selenolate (NC-NapS and NC-NapSe, respectively; see Figure 1 for the starting materials) immobilized on Au(111) as SAMs. Both systems were characterized extensively by a combination of complementary spectroscopic and microscopic techniques, demonstrating the high

quality of the monolayers and providing a reliable basis for further dedicated experiments. Of particular importance were comparable packing densities and molecular orientations in both studied systems, which, in our opinion, are indispensable prerequisites for reliable comparison of these systems regarding bond strength and transport properties. The issue of the bond strength was addressed by exchange experiments and static secondary ion mass spectroscopy (S-SIMS). The question of the charge transport properties was pursued by resonant Auger electron spectroscopy (RAES) within the core–hole–clock (CHC) approach. This contact-free method allows monitoring of charge transfer (CT) dynamics on the femtosecond time scale following a resonant excitation of a core-level electron at a specific functional group to a bound state above the Fermi level of the substrate.^{52–55} Such a dynamic is an important phenomenon on its own but is also a numerical fingerprint for the electrical transport properties of a particular molecule adsorbed on the solid support, relying on the inverse relation between the characteristic CT time and the current in a molecular junction. Significantly, the use of the CHC approach solves the problem of the top contact, along with the controversy regarding the amount of involved moieties since the results are representative of individual molecules. As a suitable functional group, serving as starting point of CT through the molecular framework to the substrate, the nitrile group ($-\text{C}\equiv\text{N}$) was utilized, following the positive experience of our previous studies.^{56–59} This was the major reason to use nitrile-substituted naphthalenes instead of nonsubstituted ones. A further reason was a presumed positive impact of the nitrile group on the long-range order in the monolayers. According to the literature, the order in the SAMs of nonsubstituted naphthalene-2-thiol is either poor⁶⁰ or only local.^{61,62} Finally, following a recently developed approach,^{63,64} the nitrile group served as a suitable spectroscopic marker to unambiguously determine molecular orientation in the systems studied.

RESULTS AND DISCUSSION

General Comments. The NC-NapS and NC-NapSe films were prepared at room (RT) and elevated (60 °C) temperature. All experiments were performed on the samples prepared at 60 °C because of their superior quality, as will be shown in the next section. The structure and molecular organization in the films were studied by scanning tunneling microscopy (STM), high-resolution X-ray photoelectron spectroscopy (HRXPS), ellipsometry, infrared reflection absorption spectroscopy (IRRAS), and angle-resolved near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. Specific questions were addressed by RAES, S-SIMS, and dedicated exchange experiments as described in the previous section.

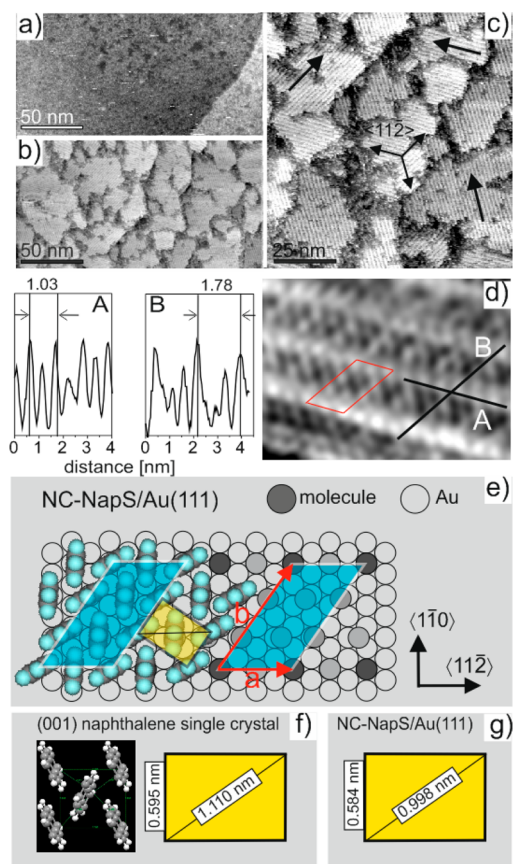


Figure 2. STM images taken with different resolutions for the NC-NapS SAMs on Au(111) prepared at room temperature (a) and at 60 °C (b–d). Height profiles A and B are taken along the lines depicted in (d); the profiles with the vertical scale included are presented in Figure S5a in the Supporting Information. The red box in (d) marks the oblique ($2\sqrt{3} \times \sqrt{37}$) unit cell schematically presented in (e). In (f), the 2D herringbone arrangement of the naphthalene molecules within the (001) plane of the naphthalene single crystal is shown, along with the respective rectangular unit cell (in yellow). A similar structural motif can be found in the STM images of the NC-NapS SAMs, as shown by the yellow rectangle in (e). The dimensions of this motif, as determined by STM, are presented in (g) for direct comparison with (f).

Scanning Tunneling Microscopy. Representative STM data obtained for the NC-NapS SAMs are presented in Figure 2. The images in Figure 2a,b, obtained from large areas, allow comparison of the overall morphology of the samples prepared at RT and 60 °C. In contrast to the rough and very defective surface observed for the sample prepared at RT (Figure 2a), the samples prepared at the elevated temperature show a distinct molecular structure with domains in the range of ~20–40 nm (Figure 2b). At higher resolutions, these well-ordered domains exhibit a characteristic stripe pattern strictly following the $\langle 11\bar{2} \rangle$ high-symmetry directions of the underlying Au(111) substrate (Figure 2c). The representative molecular resolution image shown in Figure 2d reveals that the NC-NapS SAMs form a high-density structure with a comparably large unit cell. The average dimensions of

this unit cell are $a = 1.03 \pm 0.04$ nm and $b = 1.78 \pm 0.05$ nm, as determined from the appropriate height profiles A and B in Figure 2d. Such a unit cell can be described as an oblique ($2\sqrt{3} \times \sqrt{37}$) structure, which is commensurate with the Au(111) substrate and has cell vectors of 1.00 and 1.75 nm length, respectively. With six molecules per unit cell, the molecular footprint for this structure amounts to 0.239 nm². A schematic cartoon with the possible herringbone arrangement of the NC-NapS molecules in this structure is shown in Figure 2e (for the sake of clarity, individual molecules are either presented as a phenyl ring or as a gray or black circle).

The above 2D arrangement can be compared with the crystal structure of the parent compound, naphthalene. It is well-known that naphthalene crystallizes in a monoclinic lattice with layered structure.⁶⁵ Figure 2f shows schematically the arrangement of molecules within the layers that correspond to the (001) planes. The naphthalene molecules adopt a herringbone structure with a rectangular unit cell (yellow rectangle), the shorter side of which is 0.595 nm, while its diagonal equals 1.11 nm. A similar rectangle can also be fitted into the motif of the oblique ($2\sqrt{3} \times \sqrt{37}$) structure shown in Figure 2e, with the dimensions of the shorter side and diagonal equal to 0.584 and 0.998 nm, respectively (see Figure 2g). This comparison proposes that the arrangement of NC-NapS molecules on the Au(111) surface within the ($2\sqrt{3} \times \sqrt{37}$) lattice has a certain similarity to the packing motif along the (001) plane in crystalline naphthalene.

A compilation of analogous STM data collected for the NC-NapSe monolayers on the Au(111) substrate is presented in Figure 3. As in the NC-NapS case, NC-NapSe SAMs prepared at RT are defective and unordered (Figure 3a), while the preparation at 60°C results in extended ordered structures (Figure 3b). At higher resolution, these SAMs reveal well-defined domains, which, at first sight, have a similarly striped structure and similar dimensions ($20\text{--}40$ nm, Figure 3c) as those in the NC-NapS monolayers obtained as 60°C (Figure 2c). However, in the NC-NapSe case, the stripes run along the $\langle 1\bar{1}0 \rangle$ high-symmetry directions of the Au(111) substrate, in contrast to the $\langle 11\bar{2} \rangle$ directions observed for the NC-NapS SAMs. A representative molecular resolution image shown in Figure 3d reveals that the NC-NapSe monolayers form a densely packed structure with a comparably small, rectangular unit cell. The average dimensions of this unit cell, $a = 0.61 \pm 0.03$ nm and $b = 0.75 \pm 0.05$ nm, marked in the characteristic cross sections A and B in Figure 3d, are very close to the rectangular ($2 \times 1.5\sqrt{3}$) structure of the nonreconstructed substrate, with cell dimensions of 0.58 nm $\times$ 0.75 nm, corresponding to a molecular footprint of 0.215 nm² ($\sim 11\%$ less than the value for NC-NapS/Au). Thus, presumably, the structure of the NC-NapSe monolayer mimics that of the

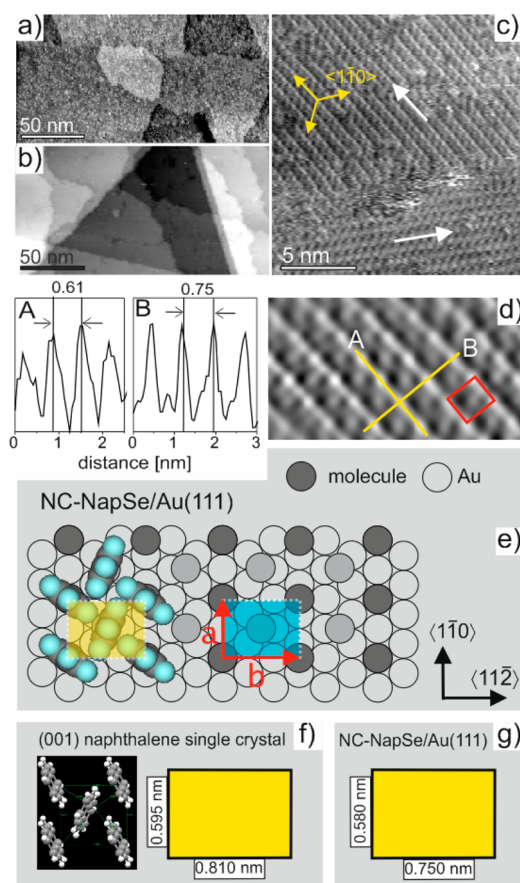


Figure 3. STM images taken with different resolutions for the NC-NapSe SAMs on Au(111) prepared at room temperature (a) and at 60°C (b–d). Height profiles A and B are taken along the lines depicted in (d); the profiles with the vertical scale included are presented in Figure S5b in the Supporting Information. The red box in (d) marks the rectangular ($2 \times 1.5\sqrt{3}$) unit cell schematically presented in (e). In (f), 2D herringbone arrangement of naphthalene molecules within the (001) plane of the naphthalene single crystal is shown, along with the respective rectangular unit cell (in yellow). A similar structural motif can be found in the STM images of the NC-NapSe SAMs, as shown by the yellow rectangle in (e). The dimensions of this motif, as determined by STM, are presented in (g) for direct comparison with (f).

nonreconstructed substrate, even though the basic ($2 \times 1.5\sqrt{3}$)*rect* unit cell is incommensurate with the substrate. As commensurate entity, a double unit cell, a ($2 \times 3\sqrt{3}$)*rect* structure, can be considered strictly within the Wood's notation. Regardless of this formality, the observed packing motif is simple and has a strong similarity to the molecular arrangement within the (001) plane of crystalline naphthalene, as shown in the cartoons in Figure 3f,g.

High-Resolution X-ray Photoelectron Spectroscopy. C 1s, N 1s, S 2p, and Se 3d HRP spectra of the NC-NapS and NC-NapSe films prepared at 60°C are presented in Figure 4. They go in line with the formation of well-defined SAMs. Indeed, the S 2p spectrum of NC-NapS/Au in Figure 4d exhibits a distinct $S 2p_{3/2,1/2}$ doublet at a binding energy (BE) position of ~ 162.0 eV ($S 2p_{3/2}$) with no traces of atomic sulfur, disulfide, unbound

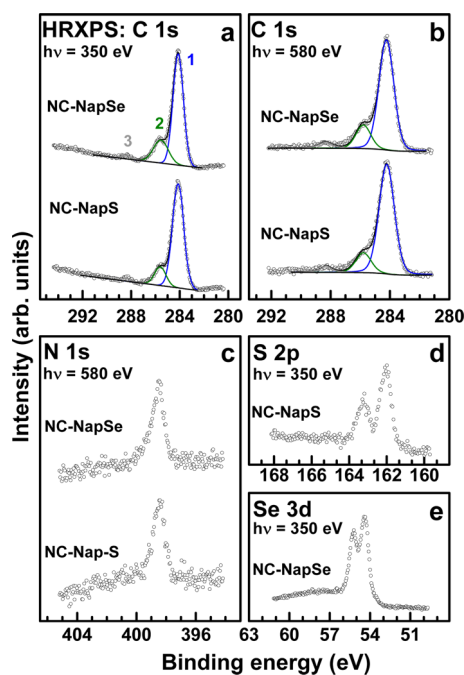


Figure 4. C 1s (a,b), N 1s (c), S 2p (d), and Se 3d (e) HRXP spectra of the NC-NapS and NC-NapSe SAMs. The C 1s spectra are decomposed in individual emissions, viz. main peak (1; blue line), high BE shoulder (2; olive line), and a low-intensity feature (3; gray line). The photon energies are given in the panels.

thiol, or oxidized species. This BE value corresponds to the thiolate species bound to noble metal surfaces,^{66–68} which suggests that basically all molecules in the NC-NapS films were anchored to the substrate *via* a thiolate–gold bond, as should be the case for well-defined SAMs. Similarly, the Se 3d spectrum of NC-NapSe/Au in Figure 4e exhibits a sole Se 3d_{5/2,3/2} doublet at a BE position of ~54.25 eV (Se 3d_{5/2}) characteristic of the selenolate species bound to noble metal surfaces.^{34,35,39,68} This means that basically all molecules in the NC-NapSe films were anchored to the substrate *via* a selenolate–gold bond, forming well-defined SAMs.

The C 1s spectra of the NC-NapS and NC-NapSe monolayers in Figure 4a,b exhibit an intense emission at a BE of 284.15 eV (1) accompanied by a weak shoulder at higher BE (285.65 eV) (2). The intense emission can be assigned to the naphthalene backbone, while the high BE shoulder can be mainly associated with the nitrile carbon, similar to the case of nitrile-substituted oligophenylenes and oligo(phenylene ethynylene)s.^{64,69} In accordance with the above assignment, the relative intensity of the shoulder decreases with increasing photon energy as follows from comparison of Figure 4a,b. This happens because the larger inelastic mean free path at higher kinetic electron energies favors photoemission from the backbone (inner part of the sample) compared to that from the tail group (outer surface of the sample). This decrease is stronger for NC-NapSe/Au than for NC-NapS/Au, which is presumably related to an admixture of a weak signal

from a minor contamination (CO) to the shoulder, with a somewhat higher contribution for NC-NapS/Au. In addition, there is a low-intensity feature at 288.3 eV (3), related presumably to another minor contamination such as COOH. The contamination was most likely located at the SAM–substrate interface since its relative weight increased with increasing kinetic energy of the photoelectrons.

The N 1s spectra of the NC-NapS and NC-NapSe SAMs in Figure 4c exhibit a single N 1s emission at a BE of 398.5 eV. This emission can be assigned to the nitrogen atom of the nitrile group, similar to the analogous systems.^{58,64,69} The presence of the single emission only suggests the same chemical state and location within the SAMs for all nitrile groups. In view of the given attachment geometry (see the discussion regarding the S 2p and Se 3d HRXP spectra), all nitrile groups are exclusively located at the SAM–ambient interface.

Apart from the above analysis of the HRXP spectra, characteristic intensity relations were considered. In particular, the C 1s/Au 4f intensity ratio for the NC-NapSe SAMs was found to be slightly higher than that for the NC-NapS monolayers at both excitation energies used (350 and 580 eV). Accordingly, the effective thickness of the former films (~1.17 nm), calculated within the standard approach,^{70,71} was found to be slightly (by ~11%) larger than that of the latter films (~1.05 nm). This suggests a slightly higher packing density of the NC-NapSe SAMs as compared to the NC-NapS monolayers, in full agreement with the STM data which give a similar difference in the molecular footprint between NC-NapSe/Au and NC-NapS/Au. Significantly, the thickness values are very close to the lengths of the NapS and NC-NapSe precursors (1.12 and 1.14 nm, respectively), implying dense molecular packing in the monolayers, once more, in agreement with the STM data.

Ellipsometry and Infrared Reflection Absorption Spectroscopy.

The HRXPS results were verified by ellipsometry. Accordingly, the thicknesses of the NC-NapS and NC-NapSe films were estimated at 1.03 ± 0.08 and 1.19 ± 0.04 nm, respectively. These values agree well with the effective thicknesses derived on the basis of the HRXPS data, corroborating the reliability of the results.

The films were further characterized by IRRAS. In Figure 5, experimental and calculated spectra of the NC-NapS and NC-NapSe species and the respective SAMs are compiled. The assignment of the bands to certain vibrational modes (see Table S1 in the Supporting Information) was performed with the help of calculated spectra of isolated nitrile-substituted naphthalenethiol and -selenoacetate molecules. The IRRAS spectra of the NC-NapS and NC-NapSe films confirm formation of well-defined monolayers. In particular, for the NC-NapSe film, the absence of bands related to the acetate moiety (2 and 5) indicates that this group has been

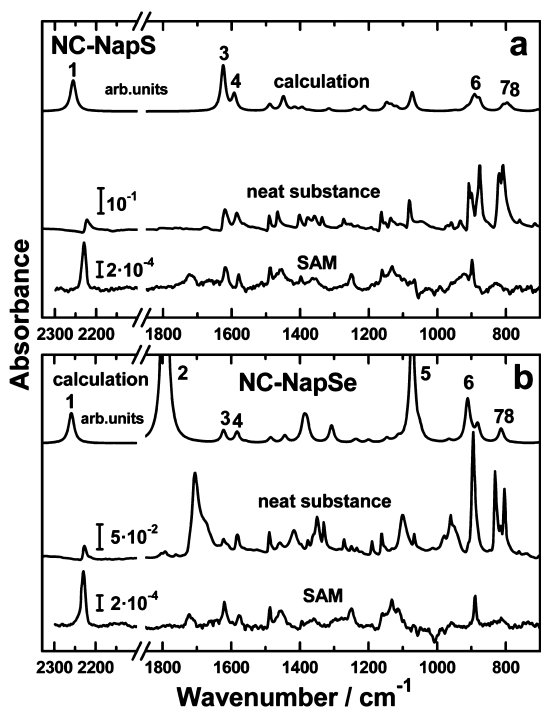


Figure 5. IR spectra for NC-NapSH/NC-NapS (a) and NC-NapSeAc/NC-NapSe (b). The upper traces represent calculated spectra of the isolated molecules using DFT; the middle traces show the spectra of the neat substances (NC-NapSH and NC-NapSeAc); in the lower traces, the IRRA spectra of the NC-NapS and NC-NapSe SAMs on Au are displayed. The theoretical spectra are scaled in arbitrary units; the scale bars for the absorbance of the experimental spectra are given in the figure. The most important vibrational bands are designated with numbers. See text for details.

cleaved off upon the formation of a gold–selenolate bond, as has been expected.⁴¹ Significantly, for both NC-NapS and NC-NapSe films, bands with out-of-plane transition dipole moments (TDMs; **7** and **8**) are clearly attenuated in comparison to bands with TDMs parallel to the C≡N bond axis (**1**, **3**, **4**, **6**). In view of the surface selection rule for metal substrates,⁷² this behavior leads to the assumption that the aromatic backbones of the NC-NapS and NC-NapSe molecules are oriented predominantly perpendicular to the substrate surface, corresponding to the entire upright orientation of the SAM constituents.

Note that the intensities of the C≡N stretch bands (**1**) in the IRRA spectra of NC-NapSe/Au are slightly larger than that in the spectra of NC-NapS/Au. This can be caused either by a somewhat more upright orientation of the NC-NapSe molecules or by a higher surface coverage, which is presumably the case in view of the STM, HRXPS, and ellipsometry data. As for the exact molecular orientation, it could be better addressed by NEXAFS spectroscopy, as will be described in the next section.

Near-Edge X-ray Absorption Fine Structure Spectroscopy.

The C K-edge NEXAFS spectra of the NC-NapS and NC-NapSe SAMs are presented in Figure 6a. This figure compiles the spectra acquired at an X-ray incidence

angle of 55° as well as the difference between the spectra acquired at X-ray incidence angles of 90 and 20°. The angle of 55° is the so-called magic angle of X-ray incidence; at this orientation, the spectrum is not affected by any effects related to molecular orientation and is therefore exclusively representative of the chemical identity of investigated samples.⁷³ In contrast, the difference of the NEXAFS spectra acquired at normal (90°) and grazing (20°) angles of X-ray incidence is a fingerprint of the linear dichroism and, thus, representative of the molecular orientation and orientational order in the system studied.

The spectra in Figure 6a exhibit a variety of overlapping absorption resonances in the pre-edge area and in the vicinity of the absorption edge. To distinguish between individual resonances, this region is presented separately in Figure 6b, along with the spectra of two reference systems, that is, SAMs of nonsubstituted naphthalene-2-thiol (NapS) and nitrile-substituted biphenylthiol (NC-BPT)^{63,64} on Au(111). The spectrum of the NC-BPT film exhibits typical features of poly-*p*-phenylenes,^{73–76} π_1^* (**1**), π_2^* (**2**), and σ_1^* (**3**) resonances of the phenyl rings at 285.0, 288.5, and 292.9 eV, respectively, along with the double π^* resonance at 286.0 and 286.7 eV (**4** and **5**) associated with the terminal benzonitrile moiety.^{58,64,69} The dominant π_1^* resonance splits into two contributions (**1a** and **1b**), at 284.65 and 285.4 eV, when passing from the NC-BPT to NapS monolayer. Such a splitting is typical for acenes^{75,77–80} and is explained by the chemical shift of the two symmetry-independent carbon atoms.⁷⁸ Apart from this splitting and the lack of the benzonitrile-related resonances (**4** and **5**), the spectrum of the NapS film mimics that of the NC-BPT SAM, exhibiting the same resonances (**2** and **3**), along with a R*/C—S* resonance at 286.8 eV. In accordance with the molecular structure, the spectra of the NC-NapS and NC-NapSe SAMs exhibit resonances characteristic of both nonsubstituted naphthalene (**1a**, **1b**, **2**, and **3**) and benzonitrile (**4** and **5**). Distinct differences are a renormalization of the relative intensities of the **1a** and **1b** resonances and an increase in the relative intensity of the major benzonitrile-related feature (**5**). These changes can be tentatively explained by the conjugation between the π^* systems of the nitrile moiety and naphthalene backbone, resulting in a redistribution of the electron density and, subsequently, in changes in the oscillator strengths of the involved electronic transitions.

The N K-edge NEXAFS spectra of the NC-NapS and NC-NapSe SAMs are presented in Figure 6c. These spectra are dominated by a double π^* resonance at ~398.8 and ~399.7 eV, accompanied by a weak feature at ~401.7 eV (presumably π_4^* of nitrile)^{81,82} and several hardly perceptible σ^* resonances at higher PEs. The double π^* resonance is characteristic of benzonitrile and observed for the gas phase,⁸² molecular solid,⁸¹ and monomolecular films containing this moiety.^{58,64,69}

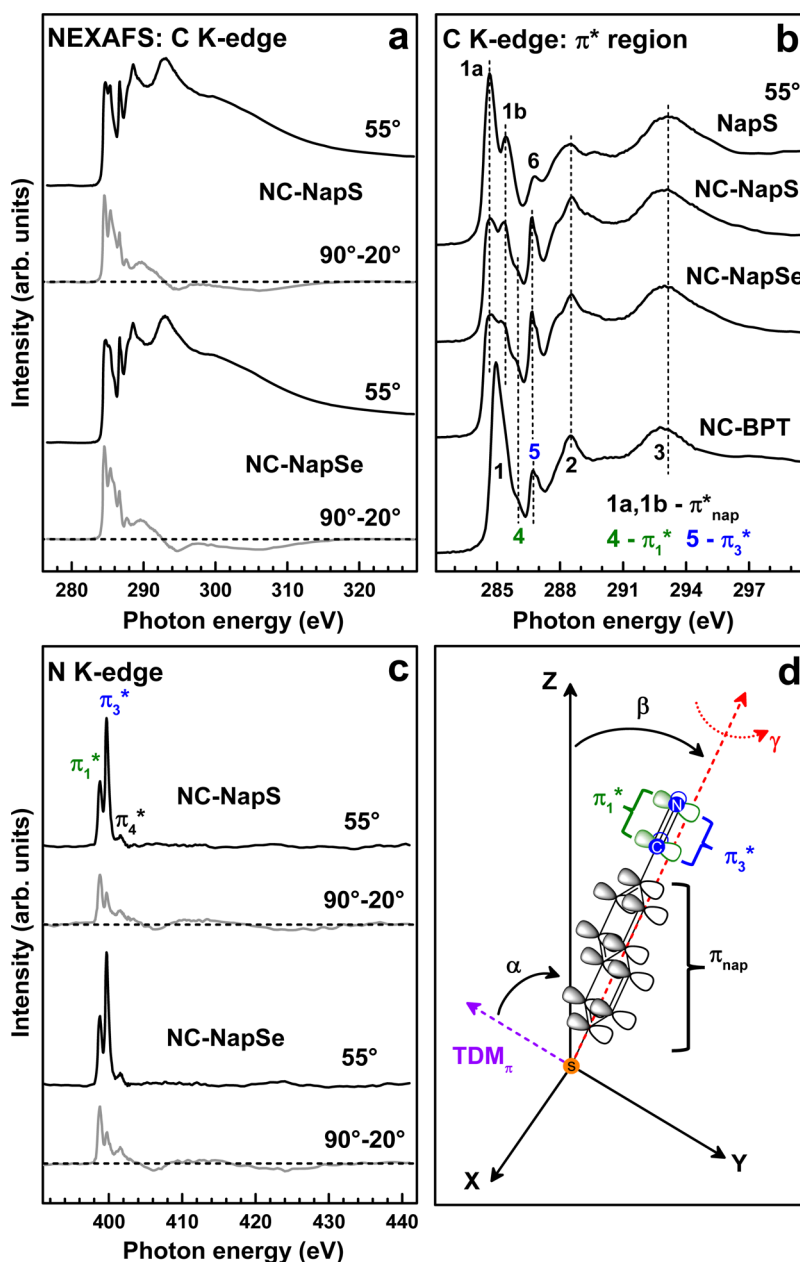


Figure 6. C (a,b) and N (c) K-edge NEXAFS spectra of the NC-NapS and NC-NapSe SAMs acquired at an X-ray incident angle of 55° (black solid curves), along with the respective difference between the spectra collected under normal (90°) and grazing (20°) incidence geometry (gray solid curves in a and c). The horizontal dashed lines correspond to zero. In (b), the region of the π^* resonances is presented, and the spectra of several reference systems such as NapS and NC-BPT SAMs are given for comparison. Individual resonances in b and c are marked, in b by numbers; see text for details. The vertical dashed lines are guides for the eye. (d) Schematic drawing of the orientation of the NC-NapS and NC-NapSe molecules in the respective SAMs. The π_{nap}^* orbitals of the naphthalene backbone (black) and the π_1^* orbital of the nitrile group (green) are parallel to each other and perpendicular to the molecular plane; the respective transition dipole moment TDM_π is shown as a violet arrow; its orientation is given by the angle α . The π_3^* orbital of the nitrile group (blue) is parallel to the molecular plane. The backbone tilt angle β and twist angle γ describe the molecular orientation. At $\gamma = 0$, TDM_π lies in the plane spanned by the z- and the molecular axis (red dashed line). Black, green, and blue are used to color-code the respective resonances in b and c.

The appearance of this resonance is related to the conjugation between the π^* orbitals of the nitrile group and the adjacent phenyl ring. As a result, the degeneration of the $\pi(\text{C}\equiv\text{N}^*)$ orbital is lifted and it splits into two orbitals with distinctly different energies (in contrast to nitrile-substituted alkanethiols where the energies are quite close),^{56,57,59} which are oriented

either perpendicular (lower PE; π_1^*) or parallel (higher PE; π_3^*) to the plane of the adjacent ring,^{81,82} as schematically shown in Figure 6d. The comparably lower intensity of the π_1^* resonance can be explained by the delocalization of the respective orbital over the entire benzonitrile moiety, whereas π_3^* is exclusively localized at the nitrile group.

TABLE 1. Average Tilt Angles of the π_{nap}^* (1 and 2) and $\pi_{1,3}^*$ (NC) Orbitals Derived from the Numerical Evaluation of the NEXAFS Data for the NC-NapS, NC-NapSe, and NapS SAMs and the Average Molecular Tilt and Twist Angles of the Molecular Backbone (Error Bars Can Be Estimated at $\pm 3^\circ$)

average angles/system	NC-NapS	NC-NapSe	NapS
π^* orbitals (naphthalene) — α_{nap}	68°	67°	71°
π_1^* orbital (NC) — α_1	66°	67°	
π_3^* orbital (NC) — α_3	57°	57°	
twist angle (γ) from α_1 and α_3	52°	54°	
molecular tilt (β) from α_1 and α_3	43°	42°	
molecular tilt (β) from α_{nap} and $\gamma(\alpha_1, \alpha_3)$	38°	41°	

The C and N K-edge NEXAFS spectra of NC-NapS and NC-NapSe SAMs exhibit pronounced linear dichroism as follows from the respective difference curves in Figure 6a,c. Considering that the TDMs associated with the dominant π^* resonances are oriented perpendicular to the molecular axis, the positive sign of the respective difference peaks suggests an upright orientation of the molecules in the SAMs. This qualitative conclusion goes in line with the one drawn from the IR spectra of these films (see above). While a quantitative evaluation of the IR data was not possible, the entire set of NEXAFS spectra could be processed self-consistently to obtain exact twist and tilt angles. Within this procedure, performed within the standard theoretical framework for vector type molecular orbitals,^{73,76} the average tilt angles of the most dominant π^* orbitals of the naphthalene backbone (**1a** and **1b**, see Figure 6b) and the nitrile moiety (π_1^* and π_3^* , see Figure 6c) were derived. They are compiled in Table 1, along with the analogous value for the reference NapS SAMs. A schematic drawing of the target molecules, along with the relevant molecular orbitals and angles, is presented in Figure 6d.

Based on the derived angle values for the NC-NapS and NC-NapSe SAMs, average tilt and twist angles for the molecular backbones in these monolayers were determined with the following equations

$$\cos(\alpha_1) = \sin(\beta)\cos(\gamma) \quad (1)$$

$$\cos(\alpha_3) = \sin(\beta)\cos(\pi/2 - \gamma) \quad (2)$$

and

$$\cos(\alpha_{\text{nap}}) = \sin(\beta)\cos(\gamma) \quad (3)$$

within the established evaluation procedure.^{63,64,69} Note that the determination of both tilt and twist of the naphthalene backbones in the target SAMs was only possible due to the attachment of the nitrile tail groups to these backbones and alignment of the orthogonal π_1^* and π_3^* orbitals of this groups with the π_{nap}^* orbitals. Without this dedicated tail group, only the average orientation of the TDM $_{\pi^*}$ can be determined. The molecular tilt can then only be

evaluated within an assumption regarding the value of the twist angle. Such an assumption, even though reasonable (e.g., based on the data for the respective bulk systems or indirect data by other techniques),¹⁷ is of course inferior to the direct determination of the twist angle, as in the present case.

The derived tilt and twist values for NC-NapS and NC-NapSe SAMs are compiled in Table 1. Significantly, the tilt angles calculated from the system of eqs 1 and 2 are very close to the analogous values calculated from eq 3. This underlines the reliability of the approach—in view of the fact that the above calculations were based on the independently determined values for the different building blocks of the target molecules, that is, the naphthalene backbone and nitrile group. According to Table 1, the average tilt and twist angles of the molecular backbones in the NC-NapS and NC-NapSe SAMs are very similar, being ~ 41 and $\sim 53^\circ$, respectively. Note that the values of the tilt angles are in accordance with the attenuation of the out-of-plane bands in the IRRA spectra of the SAMs (see above).

The relatively high tilt can be a consequence of the dipole–dipole interaction between the nitrile tail groups at the SAM–ambience interface. Minimization of this unfavorable interaction can be achieved by the tilting of the nitrile groups,^{83,84} along with the rigidly bound naphthalene backbones. Note that the non-symmetrical attachment of these backbones to the thiolate and selenolate headgroups provides an additional rotational degree of freedom for the naphthalene unit,⁶² similar to the case of anthracene-substituted alkanethiolates.⁸⁰ This permits an easy adoption of the most suitable orientation of the molecular backbones, depending on the balance of the structure–building interactions.

In agreement with the above hypothesis, the average tilt angle of the π^* orbital in the NapS monolayers is larger than those in the NC-NapS and NC-NapSe SAMs (see Table 1). This suggests a smaller molecular inclination, even at the same twist angle as for the nitrile-substituted films. At a lower twist angle, such as for the respective bulk material (25°), the molecular inclination is even smaller, being 22° , which is very close to the analogous value for the bulk naphthalene (20.5°).

Exchange Experiments. To compare the relative stability of the S–Au(111) and Se–Au(111) bonds, exchange experiments were performed by incubation of the NC-NapS or NC-NapSe SAMs formed at 60°C in ethanolic solution of hexadecanethiol (HDT) (see Methods for details). The progress of the exchange reaction was monitored by the advancing water contact angle (WCA) goniometry. The respective data obtained for the NC-NapS and NC-NapSe monolayers are summarized in Figure 7a. The WCA values for the freshly prepared films (i.e., at an incubation time of 0 h) are identical ($\sim 50^\circ$) within the measurements precision and characteristic of hydrophilic surfaces, as can be expected.

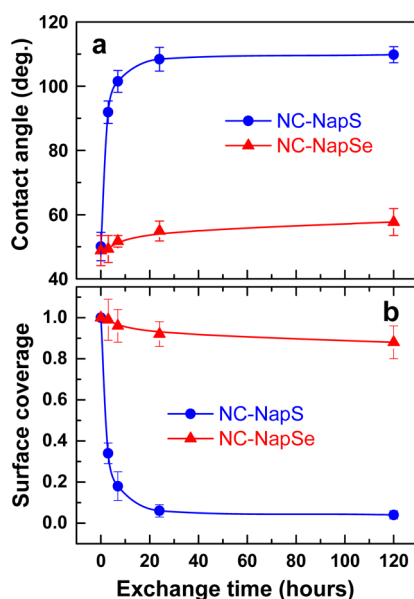


Figure 7. WCA (a) and relative surface coverage of the NC-NapS(Se) molecules (b) derived in the course of the exchange reaction between the NC-NapS (blue) or NC-NapSe (red) SAMs on Au(111) and HDT molecules in solution. The lines are guides for the eyes. See text for details.

The analysis of the WCA values as functions of the incubation time in the HDT solution shows drastic differences between the NC-NapS and NC-NapSe SAMs. Whereas, in the former case, WCA is gradually changing from its initial value of 50° toward the value of about 110°, which is very close to the WCA measured for freshly prepared HDT/Au(111) (112°), only a small change (to ~55°) is observed for the selenolate SAM. The respective change in the molecular composition as a function of the incubation time in the HDT solution was calculated on the basis of the Cassie law⁸⁵

$$\cos\theta_C = f_A \cos\theta_A + f_B \cos\theta_B; f_A + f_B = 1 \quad (4)$$

which describes the effective contact angle value θ_C for a surface covered by fractions f_A and f_B of the materials A and B, the neat surfaces of which would expose contact angle values of θ_A and θ_B , respectively. The result of the calculations, based on the data shown in Figure 7a, is presented in Figure 7b. As shown in this figure, there is a nearly complete (~95%) exchange reaction between the HDT molecules in solution and the NC-NapS moieties on Au(111). In contrast, an analogous analysis for the NC-NapSe SAMs yields an extent of exchange of only ~10% during the entire reaction time (120 h). This suggests that only the defect sites in the original film were involved before the reaction was apparently terminated, presumably due to the high stability of the densely packed selenolate–SAM structure.

Secondary Ion Mass Spectrometry. Another technique, which recently proved to be extremely powerful for the determination of relative stabilities of headgroup–substrate bonds, is static SIMS (S-SIMS).⁸⁶ As documented

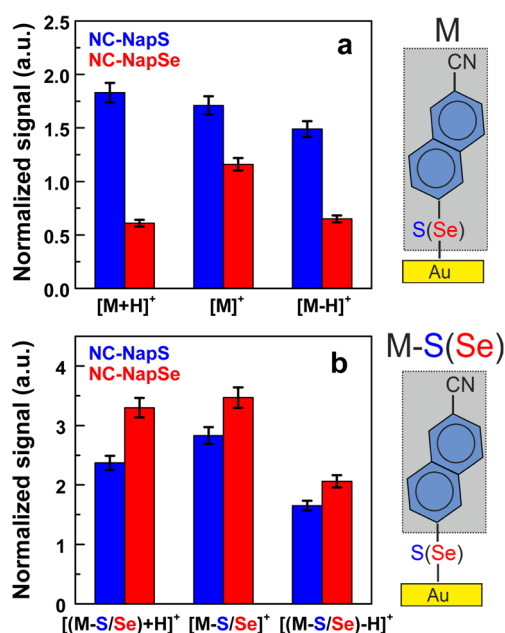


Figure 8. S-SIMS data analysis. (a) Normalized signal of the $[M+H]^+$, $[M]^+$, and $[M-H]^+$ secondary ions related to the desorption of the complete molecules for NC-NapS/Au(111) (blue bars) and NC-NapSe/Au(111) (red bars) SAMs. (b) Analogous data for the secondary ions related to the desorption of desulfurized fragments from NC-NapS/Au(111), viz. $[(M-S)+H]^+$, $[M-S]^+$, and $[(M-S)-H]^+$ (red bars) as well as deselenized fragments from NC-NapSe/Au(111), viz. $[(M-Se)+H]^+$, $[M-Se]^+$, and $[(M-Se)-H]^+$ (blue bars).

in Figure S6 in the Supporting Information, both negative and positive ion mass spectra of the NC-NapS and the NC-NapSe SAMs were recorded. These spectra exhibit secondary ion signals typical of SAMs on gold, that is, sulfur(selenium)–gold clusters (having the general form of $[Au_xS(Se)_y]^-$), different molecular fragments, and metal–molecule clusters. To gain information related to the molecule–substrate interface stability, we have focused on analyzing in detail the signals of the positive ions associated with the complete molecules ($[M]^+ = [NC-NapS(Se)]^+$) and the desulfurized (or deselenized) fragments ($[M-S(Se)]^+ = [NC-Nap]^+$) emitted as a result of the ion-impact-induced breaking of the Au–S(Se) and S(Se)–C bonds, respectively (see the schematic cartoon in Figure 8). The relative intensities of these particular ions as well as of the related ions resulting from removing or attaching a single H atom are presented in Figure 8. The comparison of these data shows that, whereas the ion-induced desorption of the complete molecule is much more efficient for the NC-NapS as compared to the NC-NapSe SAMs, the opposite relation occurs for the desulfurized and deselenized fragments, with a noticeably lower extent in the NC-NapS case.

Resonant Auger Electron Spectroscopy. As mentioned in the introduction, the issue of electronic conductance in the NC-NapS and NC-NapSe SAMs was tested by RAES

at the N K-edge within the CHC approach. As shown by the HRXPS and NEXAFS data, the nitrile groups were exclusively located at the SAM–ambient interface, being electronically connected to the substrate through the molecular framework. Thus, the CT pathway to the substrate at the resonant excitation of the nitrile group was well-defined. However, such a CT could only occur if it is energetically allowed. For efficient electron transport, the energy of the π^* resonantly excited electron at the nitrile group should be positive with respect to the Fermi level of the substrate. Accordingly, the π^* resonance excitation energy should be higher than the BE of the respective core electron. Luckily, in the case of the NC-NapS and NC-NapSe SAMs, this condition is well fulfilled for both π_1^* and π_3^* orbitals, the excitation energies of which (~ 399.7 and ~ 398.8 eV, respectively) are higher than that of the N 1s BE (398.5 eV). Thus, tail group-to-substrate transfer of the resonantly excited electron is energetically allowed for both $[N\ 1s]\pi_1^*$ and $[N\ 1s]\pi_3^*$ excitations.

As shown and described in Figure 9a, the decay of these excitations can occur in three possible ways if radiative decay is neglected. These include, first and foremost, so-called participator (P) and spectator (SP) scenarios, resulting in final states with either one hole in the region of the occupied valence (OV) states, corresponding to the P process, or two holes in the OV states but an additional electron in the unoccupied valence (UV) states, which gives in integral one hole per excited atom and corresponds to the SP process. Additionally, CT of the excited electron to the conduction band (CB) of the substrate can occur, followed by the standard Auger decay. This route leads to the final state with two holes in OV, which is nearly identical to the final state of the Auger decay in the case of nonresonant excitation, apart from subtle effects like alignment of the core hole or difference in vibrational fine structure.⁸⁷ Since all above final states are different, also in the terms of charge, the features related to the respective scenarios can be distinguished in the joint RAE spectrum as far as the target group is clearly defined and the resonant excitation does not interfere too much with the contributions from other processes (e.g., photoemission) or other functional groups within the molecule.

An important point is that, generally, one cannot distinguish between CT to the substrate, through the molecular backbone, and CT to the backbone only in the CHC experiments involving a resonantly excitable tail group. Indeed, in both cases, the excited electron is not located any more at the terminal nitrile group, leading to the electronic configuration, which is nearly identical to the final state of the Auger decay in the case of nonresonant excitation. However, for CT to the backbone only, no dependence on the length of the backbone can be expected, which is not the case for both aliphatic and aromatic SAMs with the nitrile

substitution.^{57,58} This suggests that we indeed deal with the CT to the substrate, supported also by the energetic considerations (see above).

$[N\ 1s]\pi_1^*$ and $[N\ 1s]\pi_3^*$ RAE spectra of the NC-NapS and NC-NapSe SAMs along with their reproductions by the linear combination of the purely resonant (P and SP) and nonresonant (CT) contributions are presented in Figure 9b,c, respectively. The purely resonant contributions were measured using a reference nitrile-substituted terphenylthiol (NC-TPT) monolayer on Au(111). This molecule has the same benzonitrile functional group as the NC-NapS and NC-NapSe moieties but is too long to have a perceptible CT contribution in the RAE spectrum.⁵⁸ The RAE spectra of the NC-NapS and NC-NapSe SAMs exhibit both participator and spectator contributions, with a very low spectral weight of the former component in the $[N\ 1s]\pi_3^*$ case. These spectra are very similar to the analogous spectra of other benzonitrile-terminated monomolecular films, which were analyzed in detail elsewhere.^{58,64,69}

Analysis of the $[N\ 1s]\pi_1^*$ RAE spectra in Figure 9b suggests that they contain considerable contributions from the CT route, represented as an admixture of the nonresonant spectrum to the pure resonant curves. Reconstruction of the RAE spectra by a linear combination of the nonresonant and pure resonant line shapes reproduces the experimental curves quite fairly, giving the identical portions of the nonresonant features ($\sim 21\%$), representative of CT, for both the NC-NapS and NC-NapSe SAMs. Based on these values, we can apply the main formula of the CHC approach, $\tau_{CT} = \tau_{core} (1 - P_{CT})/P_{CT}$, where τ_{core} is the known lifetime of inner shell vacancy (6.4 fs for N 1s)⁸⁸ and P_{CT} is the relative intensity of the post-CT portion in the total decay spectrum.^{52–55,89} Accordingly, the derived τ_{CT} for both NC-NapS and NC-NapSe SAMs is 24 ± 4 fs. As expected, this characteristic time is longer than the analogous value for the monolayers of nitrile-substituted phenylthiolates (NC-PT; 9 ± 3 fs)⁵⁸ but smaller than the value for the SAMs of NC-BPT (29 ± 6 fs).⁵⁸ Most important is the fact that τ_{CT} is practically identical for the NC-NapS and NC-NapSe SAMs, differing by either thiolate or selenolate binding to the substrate.

In contrast to the $[N\ 1s]\pi_1^*$ data, the $[N\ 1s]\pi_3^*$ RAE spectra of the NC-NapS and NC-NapSe SAMs, presented in Figure 9c, do not exhibit any perceptible admixture of the nonresonant line shape. These spectra are practically identical to the properly scaled pure resonant spectra. Presumably, the characteristic CT time following the $[N\ 1s]\pi_3^*$ excitation in the NC-NapS and NC-NapSe SAMs is much longer (more than 120–150 fs) than the N 1s core hole lifetime and is therefore not resolvable within the applied CHC scheme. Note that the analogous situation occurs for the NC-BPT SAMs, as well, and, consequently, is understandable in the case of the naphthalene backbone. Note also that the distinctly different τ_{CT} for the

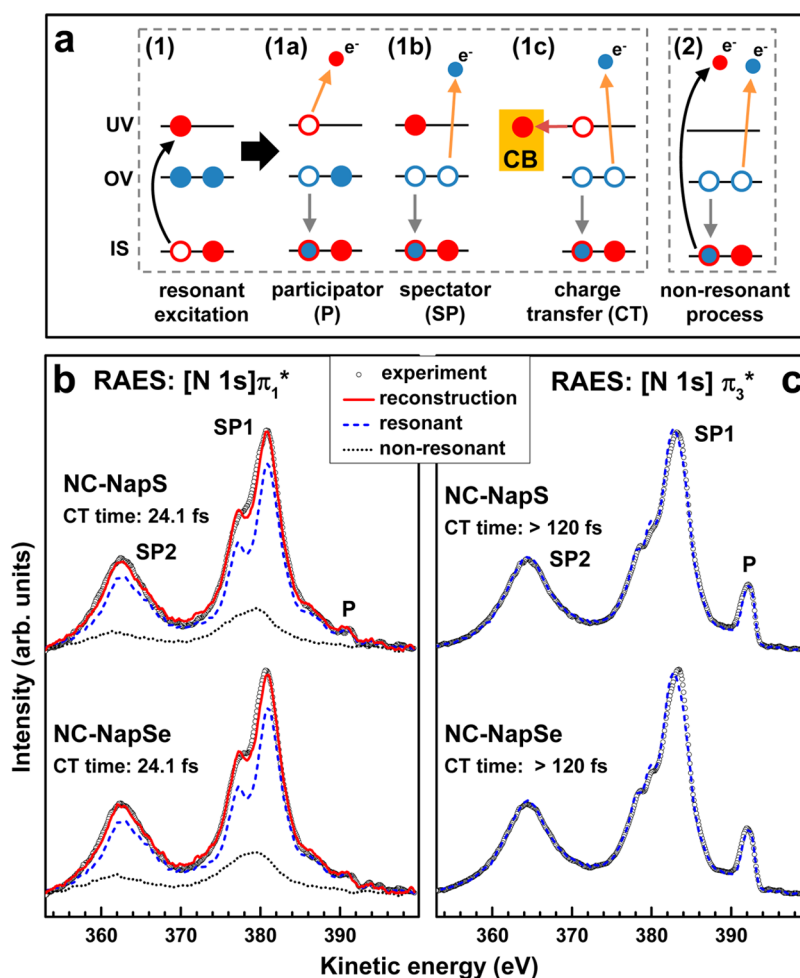


Figure 9. (a) Scheme of core excitation/de-excitation routes for the nitrile group in the NC-NapS and NC-NapSe SAMs in the framework of RAES (1). This group is considered to be weakly coupled to a continuum (e.g., substrate conduction band, CB), with IS, OV, and UV denoting inner shell (here N 1s) and occupied and unoccupied 2s- and 2p-derived valence levels, respectively. Filled and hollow circles represent electrons and holes, respectively, with red and blue color-code corresponding to IS and OV/UV, respectively. Shallow core holes as the N 1s decay nearly exclusively by an Auger process; that is, an electron from OV fills the hole (gray arrow), and a second electron carrying the excess energy is emitted (orange arrow). Upon the resonant excitation of an IS electron (black arrow in 1) into a bound state (UV), the excited electron can either take part in this decay process (participator, P) or “watch” it as a spectator (SP). Both P and SP processes lead to characteristic final states with effectively one hole in the valence region. Alternatively, CT of the excited electron to CB can occur (brown arrow), leading to the same final state with two holes in OV as the nonresonant Auger process (2), such as the excitation of an IS electron into a continuum state (black arrow in 2) followed by the emission of an OV electron. $[N\ 1s]\pi_1^*$ (b) and $[N\ 1s]\pi_3^*$ (c) RAE spectra of the NC-NapS and NC-NapSe SAMs (open circles) along with their reproductions (red solid lines in b) by the linear combination of the purely resonant (blue dashed lines) and nonresonant (black dotted lines in b) contributions. P and SP features are marked. The derived τ_{CT} values are given. The experimental and resonant spectra are almost identical in c, so that the nonresonant contribution is too small to be perceptible.

$[N\ 1s]\pi_1^*$ and $[N\ 1s]\pi_3^*$ excitations are a common phenomenon in benzonitrile-substituted monolayers.⁵⁸ This difference was explained by the different conjugations of the relevant molecular orbitals.⁵⁸ As mentioned above, the π_1^* orbital is strongly conjugated with the π^* system of the adjacent phenyl ring, which makes the electron transport along the molecular backbone more efficient. In contrast, the π_3^* orbital is almost exclusively located at the nitrile group, which can be associated with a longer CT pathway and an additional injection barrier.

DISCUSSION

We start the discussion with a summary of the basic characterization data for both systems studied, which

is a critical step to give credibility to the stability and CT dynamics experiments. When looking at the effect of the S→Se headgroup substitution on the stability and transport properties of SAMs, it is not sufficient to use just the S- and Se-based molecular analogues, as it is fulfilled in a variety of previous publications^{37,41,47,51} and also in the present case, but it needs also to be ensured that the respective SAMs formed by these analogues have similar structure and packing density, so that the relative stability and conductance data can be exclusively related to the SAM–Au(111) interface modification.

In the framework of these basic requirements, our STM analysis demonstrates that the NC-NapS and

NC-NapSe SAMs prepared on Au(111) at slightly elevated solution temperature (60 °C) exhibit well-ordered oblique ($2\sqrt{3} \times \sqrt{37}$) and rectangular ($2 \times 1.5\sqrt{3}$) molecular arrangements, respectively. Importantly, both structures are characterized by similar (within $\sim 10\%$) packing densities. These conclusions, based on the “local” STM analysis, are fully consistent with the results obtained by “large area” techniques, such as ellipsometry, IRRAS, XPS, and NEXAFS spectroscopy, which show similar effective film thicknesses (~ 10.5 and ~ 11.7 Å) as well as basically identical average tilt ($\sim 41^\circ$) and twist ($\sim 53^\circ$) angles of the molecular backbones for the both types of SAMs. Such consistency of the data obtained from the local and global techniques is crucial at this point because all further analysis of the stability and transport properties of these SAMs is based on the global techniques which sample a large area, averaging over possible structural defects.

Despite similar packing densities, the STM analysis of the NC-NapS and NC-NapSe SAMs on Au(111) also shows important structural differences. It can be assumed that, in analogy to similar systems,⁴¹ the molecules in these SAMs adopt a structure which mimics the characteristic herringbone arrangement known for crystalline naphthalene. For the NC-NapSe SAM, a simple rectangular ($2 \times 1.5\sqrt{3}$) unit cell, involving three different adsorption sites, was observed (see Figure 3e), which, within the precision of our STM measurements, corresponds directly to the molecular arrangement within the (001) plane of crystalline naphthalene. Formation of such a simple structure, close to that of crystalline naphthalene, implies that the NC-NapSe molecules are capable of achieving an optimal, single-crystal-like molecular arrangement even at the comparatively stronger interaction with the substrate. A distinctly different situation occurs in the case of the NC-NapS SAMs. Here, a somewhat larger, oblique ($2\sqrt{3} \times \sqrt{37}$) unit cell is observed, which is fully commensurate with the Au(111) substrate but is much more complex, exhibiting up to six different adsorption sites. As indicated in Figure 2e, it is still possible to fit the motif found within the (001) plane of crystalline naphthalene into the oblique ($2\sqrt{3} \times \sqrt{37}$) cell but only relying on the average distances between the molecules inside this complex structure. These observations indicate that the intermolecular interactions in the NC-NapS SAMs are inferior to the molecule–substrate interface energetics, so that the structural template provided by the substrate is a dominant factor for the structure formation. Significantly, since the packing motive and the density for both types of SAMs are very similar, we can assume that the observed difference in balancing the impact of the intermolecular interactions and molecule–substrate interface energetics on the 2D structure formation is exclusively attributed to differences in the headgroup–substrate interaction.

To learn more about the energetics of the molecule–substrate interface in both SAMs, we have conducted dedicated exchange and S-SIMS experiments probing the relative stability of these SAMs. The experiments monitoring the exchange of the NC-NapS and NC-NapSe moieties in the respective SAMs on Au(111) by HDT molecules unambiguously demonstrated an almost complete exchange reaction for NC-NapS/Au(111) and a very small extent of this process, limited, presumably, to the defect sites only, in the case of NC-NapSe/Au(111). Considering that (i) both SAMs have similar structure and packing density and that (ii) the exchange process requires the complete removal of a SAM constituent by cleaving its bond to the substrate, we conclude a higher stability of the Se–Au bond as compared to the S–Au bond in these fully aromatic SAMs with either S or Se atoms directly attached to the aromatic backbones. Importantly, the same conclusion was reached in our previous exchange experiments where the relative stability of two homologue series of biphenyl-substituted alkanethiolates and alkaneselenolates (BPnS(Se): $\text{CH}_3-(\text{C}_6\text{H}_4)_2-(\text{CH}_2)_n-\text{S(Se)}$, $n = 1-6$) on Au(111) was compared.⁴⁶ Thus, our present and previous⁴⁶ exchange experiments are complementary and show that, independent of the backbone character (aliphatic or aromatic), the Se–Au bond is more stable as compared to the S–Au one in the analogous SAMs.

To analyze the differences in stability of the molecule–substrate interface in the NC-NapS and NC-NapSe monolayers in more detail, we have exploited a novel approach based on the ion-induced desorption technique.^{86,90} The resulting data (Figure 8) suggest that, whereas the ion-induced desorption of positive ions, associated with the complete molecule and following the breaking of the Au–S(Se) bond, is much more efficient for the NC-NapS SAMs, the emission of the positive ions related to desulfurized(deselenized) fragments by breaking the S(Se)–C bond is more efficient for the NC-NapSe monolayers. Following a general logic as well as the argument provided in our recent S-SIMS publication,⁸⁶ we assume that a larger efficiency of ion-induced cleavage of a given chemical bond is related to a smaller bond energy. Consequently, our S-SIMS data indicate higher stability of the Se–Au bond as compared to the S–Au one with, at the same time, lower stability of the adjacent Se–C bond as compared to the S–C one. Such effect of reversed relative stability of these two consecutive chemical bonds (*viz.* Au–S(Se) and S(Se)–C) can be understood intuitively considering that the valence electrons of the same S(Se) atom are involved in bonding with both the Au substrate and the naphthalene moiety. A larger involvement of the valence electrons of the S(Se) atom in one of these chemical bonds should result in a smaller involvement of these electrons in the second bond, reducing, consequently, the stability of the

latter. As documented by recent studies on the model system of BPN(S(Se))/Au(111),⁸⁶ this intuitive explanation is also consistent with density functional theory (DFT) calculations of respective bond energies and molecular dynamics simulations of ion-induced desorption. A further hint is a comparison of thiolate-bonded molecules on Au, Ag, and Cu. C–S bond breaks more easily as the sulfur–metal bond gets stronger.^{91,92} Summarizing this part and taking into account the literature data for the BPN(S(Se)) monolayers,⁸⁶ we can conclude that, independent of the character of the molecular backbone (aliphatic or aromatic), the Se–Au bond is more stable as compared to the S–Au one, with, however, lower stability of the adjacent C–Se bond as compared to that of C–S.

A reasonable question at this point is why, despite the stronger binding to the substrate in the case of Se headgroup, the respective SAMs adopt a structure dictated mostly by the intermolecular interaction, with a very simple unit cell, which is very similar to the molecular arrangement in crystalline naphthalene. This unit cell involves different adsorption sites for the identical molecules (see Figure 3e), thus indicating a presumably lower involvement of the molecule–substrate energetics into the 2D ordering. There are, however, two possible explanations of this seeming contradiction. First, it can be the effect of a lower corrugation of the binding energy surface for selenolates on Au(111) as compared to thiolates,⁴⁶ which is not necessarily related to the bond strength, as occurs for alkanethiolates that have a better mobility on Ag(111) compared to Au(111), in spite of the stronger bonding to the silver substrate.¹ Second, it can be an effect of the enhanced mobility of the gold atoms in the topmost layer of the substrate mediated by the strong bond to the adsorbate molecules in the case of the Se headgroup.^{35,40,44} Indeed, it is well-known that the mobility of the atoms in the topmost layer of the substrate increases with increasing strength of the molecule–substrate bond due to the reduced interaction of the surface atoms with the underlying layers of the substrate.⁴⁶ This can then result in relaxation of the stress related to the formation of 2D incommensurate structure driven by the strong intermolecular interactions. However, the STM data for NC-NapSe/Au do not exhibit any evidence for a surface reconstruction since the molecular film, as a whole, mimics the structure of the nonreconstructed substrate, except for the small difference in the dimensions of the unit cells, related, presumably, to a limited accuracy of the STM measurements. Nevertheless, we think that the presented STM data do not allow a clear distinction between the lower corrugation and surface reconstruction scenarios, both of which are probably important.

The final part of our experiments was devoted to the analysis of the CT processes in the NC-NapS and NC-NapSe SAMs. According to the results of the dedicated

RAES-CHC measurements, the characteristic CT time (τ_{CT}) between the terminal nitrile group of the assembled NC-NapS(Se) molecules and the Au(111) substrate is essentially identical (24 ± 4 fs) for both types of SAMs. This suggests very similar CT properties for the S–Au and Se–Au bonds, even though the entire τ_{CT} is mostly determined by the molecular backbone, with the CT through the backbone being the rate-limiting step.^{57,58} Indeed, according to our previous results,^{57,58} the characteristic CT time for the S–Au bond is just 2.3–2.8 fs as far as one can disentangle this contribution from the performance of the entire molecule.⁵⁸ Thus, a certain difference between the CT performance of the S–Au and Se–Au bonds cannot be excluded, but it is certainly much lower than the factor of ~ 2.5 or even ~ 10 in relation to the entire molecule as reported in the literature.^{47,51} Note that this is the only way to deal with the charge transport/transfer properties of the S–Au and Se–Au bonds as to probe the respective molecular adsorbates as a whole and not just the S/Se–Au junction.

Significantly, the CT process in our case is related to individual molecules and does not depend on the packing density that is, however, quite close for the NC-NapS and NC-NapSe SAMs, excluding differences in matrix effects. It is also of importance that these molecules are the constituents of well-defined monolayers with similar structural and geometrical parameters. Note also that there are only a very limited number of experimental reports^{47,51} which compare electron transport through SAMs based on sulfur and selenium analogues. These studies, reporting contradictory conclusions regarding either higher⁵¹ or lower⁴⁷ conductance for the Se headgroup as compared to S one, use similar approaches based on analyzing apparent height differences in the STM images obtained for mixed SAMs of both types. Apart from the basic limitations of the applied methodology and possible role of defects, such mixed SAMs were certainly not as well-defined as the monolayers of the present study. Additional support comes from the most recent DFT calculations analyzing the influence of the S→Se headgroup substitution in biphenyl-based SAMs on gold ($C_6H_5-C_6H_4-S(Se)/Au(111)$).²² These calculations show that gold substrate work function modification due to the SAM formation, as well as HOMO and LUMO level alignment, is essentially insensitive to the S→Se substitution, which is consistent with a similar CT efficiency observed for both types of SAMs in our experiments.

Following a recent line of arguments⁴⁸ connecting the strength of the S(Se)–Au bond with the overlap and involvement of the relevant electronic states, we get a link between the results of the experiments probing this bond strength (exchange and S-SIMS) with the conclusions regarding the CT properties of the SAM studied (RAES-CHC). Along these lines,

considering higher stability of the Au–Se bond compared to that of Au–S, concluded in our study, one would presumably expect noticeable differences in the CT properties. This was not observed in our RAES-CHC experiments, but at the same time, we demonstrated that the larger involvement of the headgroup atom in binding with the metal substrate occurs at the expense of the decreased involvement in the binding with the neighboring carbon atom. Since the tunneling process involves both C–S(Se) and S(Se)–Au bonds, we suppose that the better tunneling conditions in the latter case are compensated by the worse tunneling conditions in the former case. Thus, it looks as though the S→Se substitution causes a redistribution of the electronic states at the Au–S–C interface, which, on the average, does not change the total probability of charge carrier tunneling.

CONCLUSIONS

To understand the impact of the headgroup atom substitution on structure, stability, and charge transfer properties of SAMs, two representative model systems, NC-NapS/Au(111) and NC-NapSe/Au(111), were investigated.

As a starting point, we analyzed and compared in detail the structure and molecular organization in these monolayers using both microscopic and spectroscopic techniques. The SAMs were found to be of high quality and, what was particularly important in the context of the present study, possessed the same basic structural motif (close to $(2 \times 1.5\sqrt{3})_{\text{rect}}$) as well as similar packing density (0.239 and 0.215 nm²/molecule) and molecular orientation (a tilt angle of 41–42°). These characteristics allowed for rational comparison of the bond stability at the molecule–metal interface as well as for a comparison study of CT properties of thiolate and selenolate SAMs on noble metal substrates.

Consequently, by probing this interface by the dedicated exchange experiments and, independently,

by S-SIMS technique, we demonstrated that the Au–Se bond is more stable than the Au–S one with, at the same time, lower stability of Se–C bond as compared to that of S–C, due to a redistribution of the electron density between these two adjacent bonds.

Finally, we probed the dynamic CT properties of the NC-NapS and NC-NapSe SAMs and found similar CT time for the both systems, which, in view of the well-defined monolayers with similar molecular organization and the single-molecule character of the CT process involved, suggest, in contrast to the previous studies, similar electronic coupling efficiency of the S and Se anchors.

Considering the bond stability as a measure of its strength and as a fingerprint for the overlap and involvement of the relevant electronic states, the exchange and S-SIMS results were correlated with the CT dynamics findings. Along these lines, consideration of the S–Au and Se–Au bonds alone leads, obviously, to a wrong conclusion regarding the electronic coupling efficiency of the S and Se anchors since the latter bond seems to be noticeably stronger. Instead, both S(Se)–Au and S(Se)–C bonds should be considered together. Since a comparably stronger Se–Au bond is accompanied by the weakening of the adjacent Se–C bond, the joint effect is comparable with the Au–S–C linker. This explains the equivalent CT dynamics properties of the NC-NapS and NC-NapSe SAMs found in this work and suggests that the S→Se substitution does not result in any improvement of the electronic coupling to the substrate. This observation of an independence of the CT properties on the exact interface chemistry goes in line with recently reported data for a different set of headgroup–substrate interactions.^{93,94}

However, the S→Se substitution is certainly of importance for the molecular organization and structural perfection in the given SAMs. At least in the case of the aromatic SAMs, the Se–Au bond allows for a better structural perfection as compared to the thiolate anchor, resulting in monolayers of a higher quality.

METHODS

SAMs of chalcogenolates (thiolates, selenolates) are typically formed from the respective chalcogenols or the dichalcogenides. While aromatic thiols such as 6-cyanonaphthalene-2-thiol (NC-NapSH) are usually quite stable in air, the respective selenols easily oxidize. Based on the observation that selenoacetates can form well-ordered selenolate SAMs on Au(111) equally efficiently,⁴¹ we used the air-stable 6-cyanonaphthalene-2-selenoacetate (NC-NapSeAc) as the SAM-forming molecule in this study. Due to the structural similarity, the two investigated molecules were prepared from a common intermediate, 2-bromo-6-cyanonaphthalene. This compound has been synthesized following a literature procedure,⁹⁵ starting from commercially available 2-bromo-6-naphthoic acid *via* the respective amide, which was dehydrated to the nitrile by action of trifluoroacetic acid anhydride (see Scheme S1 in the Supporting Information). Both, the bromoamide and the bromonitrile

could be crystallized to obtain their solid-state structure (see the Supporting Information for details). The introduction of the selenium atom followed a recently reported protocol, which uses a sterically hindered silaselenol for the palladium-catalyzed formation of the C–Se bond.^{96,97} The Se atom was then deprotected by the action of fluoride followed by a reprotection with acetyl chloride. A similar approach was used for the synthesis of the thiol compound by modifying previously developed protocols.^{98–101} By using a silathiol, first C–S bond formation was achieved, followed by proton-induced S–Si bond cleavage. Both NC-NapSH and NC-NapSeAc turned out to be sufficiently air-stable to be handled under the typical SAM deposition conditions. Additional details can be found in the Supporting Information.

NapS used as a reference for the spectroscopic experiments and HDT used as substituent for the substitution experiments were purchased from Sigma-Aldrich and used as received. The NC-BPT and NC-TPT used as references for the spectroscopic

experiments were synthesized according to literature.⁶³ The substrates for the SAM preparation were purchased from Georg Albert PVD, Heidelberg, Germany. They represented epitaxial Au (99.99% purity) layers of 200 nm thickness, evaporated with a rate of 2 nm/s onto the mica slides held at 340 °C. The substrates were flame-annealed before immersion into solutions of the target compounds. This procedure yielded high-quality Au films with flat terraces of several 100 nm, exhibiting a (111) surface orientation with a typical surface reconstruction pattern.¹⁰²

The NC-NapS and NC-NapSe SAMs were formed by immersion of freshly prepared gold substrates into a 1 mM solution of the above compounds in absolute ethanol for 24 h at room temperature (RT = 21 °C) or at elevated temperature (60 °C). After immersion, the SAM samples were carefully rinsed with the solvent, blown dry with argon, and either characterized immediately or kept for several days in argon-filled glass containers until the characterization at the synchrotron (see below). The reference NapS monolayers were fabricated in a similar fashion; the reference NC-BPT SAMs were prepared according to an established procedure.^{58,64}

The fabricated films were characterized by STM, HRXPS, ellipsometry, IRRAS, NEXAFS spectroscopy, RAES, S-SIMS, and dedicated exchange experiments. All experiments were performed on the samples prepared at 60 °C because of their superior quality.

For ellipsometric characterization of the monolayers, a SenTech SE 400 ellipsometer with a He–Ne laser (wavelength 632.8 nm) was used. The angle of incidence was 70° with respect to the sample surface normal. The complex refractive indices of the Au substrates were measured before SAM deposition. The extinction coefficients and the refractive indices of the monolayers were assumed to be 0 and 1.55, respectively.

IR spectra of neat substances (reference) and SAMs were recorded using a Thermo Nicolet 6700 Fourier transform IR spectrometer purged with dried and CO₂-free air and equipped with a narrow band mercury cadmium telluride semiconductor detector. All spectra were recorded at 4 cm^{−1} resolution. Neat substance spectra were obtained using a single-reflection diamond attenuated total reflection unit. IRRAS of the SAMs was carried out with p-polarized radiation at 80° relative to the sample surface normal. Perdeuterated dodecanethiolate SAMs on gold served as reference for the IRRAS measurements. Since the C–D stretch bands interfered with the C≡N stretch signal of the samples, additional spectra were recorded with a nondeuterated HDT SAM as background. Vibrational mode assignments and identification of the TDM orientations were carried out with the help of DFT calculations of single molecules IR spectra at the BP86/SVP level.

STM measurements were carried out in air at room temperature using a MultiMode IIIa Digital Instruments microscope. In all cases, tips were prepared mechanically by cutting a 0.25 mm Pt/Ir alloy (8:2, Goodfellow) wire. The data were collected in constant current mode using tunneling currents in a range of 15–40 pA and a sample bias of 0.2–0.8 V (tip positive). No tip-induced changes were observed under these imaging conditions.

The HRXPS, NEXAFS, and RAES measurements were conducted at the MAX II storage ring at the MAX-IV laboratory in Lund, Sweden, using the bending magnet beamline D1011 (plane grating monochromator) and an experimental station equipped with a SCIENTA SES200 electron energy analyzer and a partial electron yield (PEY) detector. The experiments were carried out under UHV conditions at a base pressure <1.5 × 10^{−10} mbar. Special care, including a limited exposure of a particular spot as well as control measurements, was taken to avoid damage induced by X-rays.^{68,103}

The HRXP spectra were collected in normal emission geometry for the Au 4f, Se 3d, S 2p, C 1s, and N 1s ranges. In addition, the O 1s range was monitored. The energy resolution was better than 100 meV (about 60 meV for most of the spectra), allowing a clear separation of individual spectral components. The BE scale of every spectrum was individually calibrated to the Au 4f_{7/2} emission line of the underlying Au substrate at 84.0 eV.¹⁰⁴ As far as this was necessary, the spectra were fitted by symmetric Voigt functions and a Shirley-type background. To fit

the Se 3d_{5/2,3/2} and S 2p_{3/2,1/2} doublets, we used a pair of such peaks with the same fwhms values, branching ratios of 3:2 (Se 3d_{5/2,3/2}) and 2:1 (S 2p_{3/2,1/2}), and spin–orbit splittings (verified by fit) of ~0.86 eV (Se 3d_{5/2,3/2}) and ~1.18 eV (S 2p_{3/2,1/2}).¹⁰⁴

The NEXAFS spectra were acquired at the carbon and nitrogen K-edges in the PEY acquisition mode with retarding voltages of −150 and −300 V, respectively. Linearly polarized synchrotron light with a polarization factor of ~95% was used. The energy resolution was better than 100 meV. The incidence angle of X-rays was varied from 90° (*E* vector in the surface plane) to 20° (*E* vector near the surface normal) in steps of 10–20° to monitor the molecular orientation in the SAMs. This approach is based on the dependence of the cross section of the resonant photoexcitation process on the orientation of the electric field vector of the synchrotron light with respect to the molecular orbital of interest (so-called linear dichroism in X-ray absorption).⁷³ Raw NEXAFS spectra were normalized to the incident photon flux by division through a spectrum of a clean, freshly sputtered gold sample. Subsequently, the spectra were reduced to the standard form by subtracting a linear pre-edge background and normalizing to the unity edge jump (determined by a nearly horizontal plateau 40–50 eV above the respective absorption edges). The energy scale was calibrated by means of the most intense π^* resonance of highly oriented pyrolytic graphite at 285.38 eV¹⁰⁵ in combination with the well-known $\Delta h\nu \propto (h\nu)^{3/2}$ behavior of plane grating monochromators.¹⁰⁶ The resulting energy positions are expected to be accurate and reproducible within ±0.05 eV.

The RAES spectra were acquired at the N K-edge using a SCIENTA SES200 electron energy analyzer. The X-ray incidence angle was set to 55° to suppress orientational effects;^{73,87} the take off angle of the electrons was close to normal emission. The resonant excitation energies were determined in the preliminary NEXAFS experiments. In addition, nonresonant Auger electron spectra were recorded at an excitation energy of 5–6 eV above the absorption edge. This setting seems to be optimal for nitrile-substituted SAMs on Au in order to maximize the signal-to-noise ratio and to avoid appearance of interfering gold photoemission in the spectra.⁵⁶ Finally, for every sample, a reference spectrum for the pre-edge excitation was measured. This spectrum was subtracted from the RAES and nonresonant AES spectra to correct them for a contribution of the photoemission, which could not be avoided completely.

The relative stability of the headgroup–substrate bonds in the NC-NapS and NC-NapSe monolayers was probed by dedicated exchange experiments. The above SAMs were immersed in the 1 mM ethanolic solution of HDT at room temperature. The progress of the exchange reaction was monitored for a given sample by the consecutive control of the advancing water contact angle. The measurements were carried out with a Rame-Hart goniometer, model 200, using ultrapure water (~18 MΩ). The experiments were performed under ambient conditions (temperature = 21 °C, humidity = 25%), with the needle tip in contact with the drop. Averaged values of at least 50 measurements at different locations on each sample are reported.

The SIMS experiments were performed using a TOF SIMS V system (ION TOF GmbH, Germany). The instrument was operated at a base pressure of 6 × 10^{−10} mbar. The primary 30 keV Bi⁺ ion beam was scanned over a 500 μm × 500 μm area during the data acquisition. All spectra were collected in the static SIMS regime using a total ion dose of up to 8 × 10¹⁰ ions/cm² which, for these kinds of SAMs, ensures analysis with negligible ion-induced damage, as documented by our previous studies.¹⁰⁷ The secondary ions were extracted into a reflectron time-of-flight mass spectrometer before reaching the MCP detector. For each type of SAM, three different areas on three different samples were examined with a reproducibility of ~10% in the peak intensities. Before analysis, all spectra were normalized to the respective total count numbers.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Synthetic details for the NC-NapS and NC-NapSe precursors, X-ray structures of some intermediates, tabulated IR data, and representative SIMS

spectra for the NC-NapS and NC-NapSe SAMs on Au(111). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Acknowledgment. We thank the Max-IV staff, and A. Preobrajenski, in particular, for the technical support during the synchrotron-based experiments, as well as Prof. Marek Szymonski for providing access to the STM at the Department of Physics of Nanostructures and Nanotechnology at the Jagiellonian University. This work was supported financially by the Deutsche Forschungsgemeinschaft (Grants ZH 63/14-2 and MAP B.1.4), the National Science Centre Poland (Grant DEC-2013/10/E/ST5/00060), and by funding from the European Community's Seventh Framework Programme (FP7/2007-2013) CALIPSO under Grant Agreement No. 312284. The S-SIMS equipment was purchased with the financial support of the European Regional Development Fund (Grant POIG.02.02.00-12-023/08). We also wish to acknowledge the generous gifts of gold by Umicore, Hanau, Germany, and trifluoroacetic anhydride by Solvay Fluor GmbH, Hannover, Germany.

REFERENCES AND NOTES

- Ulman, A. Formation and Structure of Self-Assembled Monolayers. *Chem. Rev.* **1996**, *96*, 1533–1554.
- Schreiber, F. Self-Assembled Monolayers: From 'Simple' Model Systems to Biofunctionalized Interfaces. *J. Phys.: Condens. Matter* **2004**, *16*, R881–R900.
- Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chem. Rev.* **2005**, *105*, 1103–1169.
- Schreiber, F. Structure and Growth of Self-Assembling Monolayers. *Prog. Surf. Sci.* **2000**, *65*, 151–256.
- McGuinness, C. L.; Diehl, G. A.; Blasini, D.; Smilgies, D.-M.; Zhu, M.; Samarath, N.; Weidner, T.; Ballav, N.; Zharnikov, M.; Allara, D. L. Molecular Self-Assembly at Bare Semiconductor Surfaces: Cooperative Substrate-Molecule Effects in Octadecanethiolate Monolayer Assemblies on GaAs (111), (110), and (100). *ACS Nano* **2010**, *4*, 3447–3465.
- Fenter, P.; Eisenberger, P.; Liang, K. S. Chain-Length Dependence of the Structures and Phases of $\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}$ Self-Assembled on Au(111). *Phys. Rev. Lett.* **1993**, *70*, 2447–2450.
- Fenter, P.; Eberhardt, A.; Eisenberger, P. Self-Assembly of *n*-Alkyl Thiols as Disulfides on Au(111). *Science* **1994**, *266*, 1216–1218.
- Poirier, G. E.; Tarlov, M. J. The $c(4 \times 2)$ Superlattice of *n*-Alkanethiol Monolayers Self-Assembled on Au(111). *Langmuir* **1994**, *10*, 2853–2856.
- Leung, T. Y. B.; Schwartz, P.; Scoles, G.; Schreiber, F.; Ulman, A. Structure and Growth of 4-Methyl-4'-mercaptobiphenyl Monolayers on Au(111): A Surface Diffraction Study. *Surf. Sci.* **2000**, *458*, 34–52.
- Fuxen, C.; Azzam, W.; Arnold, R.; Witte, G.; Terfort, A.; Wöll, C. Structural Characterization of Organothioliolate Adlayers on Gold: The Case of Rigid, Aromatic Backbones. *Langmuir* **2001**, *17*, 3689–3695.
- Ishida, T.; Mizutani, W.; Azebara, H.; Sato, F.; Choi, N.; Akiba, U.; Fujihira, M.; Tokumoto, H. Adsorption Processes of Self-Assembled Monolayers Made from Terphenyl Thiols. *Langmuir* **2001**, *17*, 7459–7463.
- Azzam, W.; Fuxen, C.; Birkner, A.; Rong, H.-T.; Buck, M.; Wöll, Ch. Coexistence of Different Structural Phases in Thioaromatic Monolayers on Au(111). *Langmuir* **2003**, *19*, 4958–4968.
- Bashir, A.; Azzam, W.; Rohwerder, M.; Terfort, A. Polymorphism in Self-Assembled Terphenylthiolate Monolayers on Au(111). *Langmuir* **2013**, *29*, 13449–13456.
- Fenter, P.; Eisenberger, P.; Li, J.; Camillone, N., III; Bernasek, S.; Scoles, G.; Ramanarayanan, T. A.; Liang, K. S. Structure of Octadecyl Thiol Self-Assembled on the Silver(111) Surface: An Incommensurate Monolayer. *Langmuir* **1991**, *7*, 2013–2016.
- Rieley, H.; Kendall, G. K.; Jones, R. G.; Woodruff, P. X-ray Studies of Self-Assembled Monolayers on Coinage Metals. 2. Surface Adsorption Structures in 1-Octanethiol on Cu(111) and Ag(111) and their Determination by the Normal Incidence X-ray Standing Wave Technique. *Langmuir* **1999**, *15*, 8856–8866.
- Zharnikov, M.; Frey, S.; Rong, H.; Yang, Y. J.; Heister, K.; Buck, M.; Grunze, M. The Effect of Sulfur-Metal Bonding on the Structure of Self-Assembled Monolayers. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3359–3362.
- Rong, H. T.; Frey, S.; Yang, Y. J.; Zharnikov, M.; Buck, M.; Wühn, M.; Wöll, Ch.; Helmchen, G. On the Importance of the Headgroup Substrate Bond in Thiol Monolayers: A Study of Biphenyl-Based Thiols on Gold and Silver. *Langmuir* **2001**, *17*, 1582–1593.
- Shaporenko, A.; Brunnbauer, M.; Terfort, A.; Grunze, M.; Zharnikov, M. Structural Forces in Self-Assembled Monolayers: Terphenyl-Substituted Alkanethiols on Noble Metal Substrates. *J. Phys. Chem. B* **2004**, *108*, 14462–14469.
- Shaporenko, A.; Müller, J.; Weidner, T.; Terfort, A.; Zharnikov, M. Balance of Structure-Building Forces in Selenium-Based Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2007**, *129*, 2232–2233.
- von Wrochem, F.; Gao, D.; Scholz, F.; Nothofer, H.-G.; Nelles, G.; Wessels, J. M. Efficient Electronic Coupling and Improved Stability with Dithiocarbamate-Based Molecular Junctions. *Nat. Nanotechnol.* **2010**, *5*, 618–624.
- Karthäuser, S. Control of Molecule-Based Transport for Future Molecular Devices. *J. Phys.: Condens. Matter* **2011**, *23*, 1–16.
- Heimel, G.; Romaner, L.; Zojer, E.; Bredas, J.-L. Toward Control of the Metal-Organic Interfacial Electronic Structure in Molecular Electronics: A First-Principles Study on Self-Assembled Monolayers of π -Conjugated Molecules on Noble Metals. *Nano Lett.* **2007**, *7*, 932–940.
- Weidner, T.; Shaporenko, A.; Müller, J.; Höltig, M.; Terfort, A.; Zharnikov, M. Self-Assembled Monolayers of Aromatic Tellurides on (111)-Oriented Gold and Silver Substrates. *J. Phys. Chem. C* **2007**, *111*, 11627–11635.
- Samant, M. G.; Brown, C. A.; Gordon, J. G., II. Formation of an Ordered Self-Assembled Monolayer of Docosaneselenol on Gold(111)-Structure by Surface X-ray-Diffraction. *Langmuir* **1992**, *8*, 1615–1618.
- Dishner, M. H.; Hemminger, J. C.; Feher, F. J. Scanning Tunneling Microscopy Characterization of Organoselenium Monolayers on Au(111). *Langmuir* **1997**, *13*, 4788–4790.
- Bandyopadhyay, K.; Vijayamohanan, K. Formation of a Self-Assembled Monolayer of Diphenyl Diselenide on Polycrystalline Gold. *Langmuir* **1998**, *14*, 625–629.
- Huang, F. K.; Horton, R. C., Jr.; Myles, D. C.; Garrell, R. L. Selenolates as Alternatives to Thiolates for Self-Assembled Monolayers: A SERS Study. *Langmuir* **1998**, *14*, 4802–4808.
- Bandyopadhyay, K.; Vijayamohanan, K.; Venkataramanan, M.; Pradeep, T. Self-Assembled Monolayers of Small Aromatic Disulfide and Diselenide Molecules on Polycrystalline Gold Films: A Comparative Study of the Geometrical Constraint Using Temperature-Dependent Surface-Enhanced Raman Spectroscopy, X-ray Photoelectron Spectroscopy, and Electrochemistry. *Langmuir* **1999**, *15*, 5314–5322.
- Nakano, K.; Sato, T.; Tazaki, M.; Takagi, M. Self-Assembled Monolayer Formation from Decaneselenol on Polycrystalline Gold As Characterized by Electrochemical Measurements, Quartz-Crystal Microbalance, XPS, and IR Spectroscopy. *Langmuir* **2000**, *16*, 2225–2229.
- Han, S. W.; Lee, S. J.; Kim, K. Self-Assembled Monolayers of Aromatic Thiol and Selenol on Silver: Comparative Study of Adsorptivity and Stability. *Langmuir* **2001**, *17*, 6981–6987.
- Yee, C. K.; Ulman, A.; Ruiz, J. D.; Parikh, A.; White, H.; Rafailovich, M. Alkyl Selenide- and Alkyl Thiolate-Functionalized

- Gold Nanoparticles: Chain Packing and Bond Nature. *Langmuir* **2003**, *19*, 9450–9458.
32. Monnell, J. D.; Stapleton, J. J.; Jackiw, J. J.; Dunbar, T.; Reinerth, W. A.; Dirk, S. M.; Tour, J. M.; Allara, D. L.; Weiss, P. S. Ordered Local Domain Structures of Decaneselenolate and Dodecane-selenolate Monolayers on Au{111}. *J. Phys. Chem. B* **2004**, *108*, 9834–9841.
 33. Sato, Y.; Mizutani, F. Formation and Characterization of Aromatic Selenol and Thiol Monolayers on Gold: *In-Situ* IR Studies and Electrochemical Measurements. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1328–1331.
 34. Shaporenko, A.; Ulman, A.; Terfort, A.; Zharnikov, M. Self-Assembled Monolayers of Alkaneselenols on (111) Gold and Silver. *J. Phys. Chem. B* **2005**, *109*, 3898–3906.
 35. Shaporenko, A.; Cyganik, P.; Buck, M.; Terfort, A.; Zharnikov, M. Self-Assembled Monolayers of Aromatic Selenols on Noble Metal Substrates. *J. Phys. Chem. B* **2005**, *109*, 13630–13638.
 36. Shaporenko, A.; Cyganik, P.; Buck, M.; Ulman, A.; Zharnikov, M. Self-Assembled Monolayers of Semifluorinated Alkaneselenolates on Noble Metal Substrates. *Langmuir* **2005**, *21*, 8204–8213.
 37. Käfer, D.; Bashir, A.; Witte, G. J. Interplay of Anchoring and Ordering in Aromatic Self-Assembled Monolayers. *Phys. Chem. C* **2007**, *111*, 10546–10551.
 38. Weidner, T.; Shaporenko, A.; Ballav, N.; Ulman, A.; Zharnikov, M. Modification of Alkaneselenolate Monolayers by Low-Energy Electrons. *J. Phys. Chem. C* **2008**, *112*, 1191–1198.
 39. Weidner, T.; Shaporenko, A.; Müller, J.; Schmid, M.; Cyganik, P.; Terfort, A.; Zharnikov, M. The Effect of the Bending Potential on Molecular Arrangement in Alkaneselenolate Self-Assembled Monolayers. *J. Phys. Chem. C* **2008**, *112*, 12495–12506.
 40. Cyganik, P.; Szelągowska-Kunstman, K.; Terfort, A.; Zharnikov, M. Odd-Even Effect in Molecular Packing of Biphenyl-Substituted Alkaneselenolate Self-Assembled Monolayers on Au(111)—Scanning Tunneling Microscopy Study. *J. Phys. Chem. C* **2008**, *112*, 15466–15473.
 41. Bashir, A.; Käfer, D.; Müller, J.; Wöll, C.; Terfort, A.; Witte, G. Selenium as a Key Element for Highly Ordered Aromatic Self-Assembled Monolayers. *Angew. Chem., Int. Ed.* **2008**, *47*, 5250–5252.
 42. Track, A. M.; Rissner, F.; Heimerl, G.; Romaner, L.; Käfer, D.; Bashir, A.; Ränger, G. M.; Hofmann, O. T.; Bucko, T.; Witte, G.; et al. Simultaneously Understanding the Geometric and Electronic Structure of Anthraceneselenolate on Au(111): A Combined Theoretical and Experimental Study. *J. Phys. Chem. C* **2010**, *114*, 2677–2684.
 43. Hohman, J. N.; Kim, M.; Schüpbach, B.; Kind, M.; Thomas, J. C.; Terfort, A.; Weiss, P. S. The Dynamic Double Lattice of 1-Adamantaneselenolate Self-Assembled Monolayers on Au{111}. *J. Am. Chem. Soc.* **2011**, *133*, 19422–19431.
 44. Dendzik, M.; Terfort, A.; Cyganik, P. Odd–Even Effect in the Polymorphism of Self-Assembled Monolayers of Biphenyl-Substituted Alkaneselenolates on Au(111). *J. Phys. Chem. C* **2012**, *116*, 19535–19542.
 45. Hohman, J. N.; Thomas, J. C.; Zhao, Y.; Auluck, H.; Kim, M.; Visselaar, W.; Kommeren, S.; Terfort, A.; Weiss, P. S. Exchange Reactions between Alkanethiolates and Alkaneselenols on Au{111}. *J. Am. Chem. Soc.* **2014**, *136*, 8110–8121.
 46. Szelągowska-Kunstman, K.; Cyganik, P.; Schüpbach, B.; Terfort, A. Relative Stability of Thiol and Selenol Based SAMs on Au(111) - Exchange Experiments. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4400–4406.
 47. Monnell, J. D.; Stapleton, J. J.; Dirk, S. M.; Reinerth, W. A.; Tour, J. M.; Allara, D. L.; Weiss, P. S. Relative Conductances of Alkaneselenolate and Alkanethiolate Monolayers on Au(111). *J. Phys. Chem. B* **2005**, *109*, 20343–20349.
 48. Yokota, K.; Taniguchi, M.; Kawai, T. Control of Electrode–Molecule Interface for Molecular Devices. *J. Am. Chem. Soc.* **2007**, *129*, 5818–5819.
 49. Di Ventra, M.; Lang, N. D. Transport in Nanoscale Conductors from First Principles. *Phys. Rev. B* **2001**, *65*, 045402.
 50. Di Ventra, M.; Lang, N. D.; Pantelides, S. T. Electronic Transport in Single Molecules. *Chem. Phys.* **2002**, *281*, 189–198.
 51. Patrone, L.; Palacin, S.; Charlier, J.; Armand, F.; Bourgoin, J. P.; Tang, H.; Gauthier, S. Evidence of the Key Role of Metal–Molecule Bonding in Metal–Molecule–Metal Transport Experiments. *Phys. Rev. Lett.* **2003**, *91*, 096802.
 52. Brühwiler, P. A.; Karis, O.; Mårtensson, N. Charge-Transfer Dynamics Studied Using Resonant Core Spectroscopies. *Rev. Mod. Phys.* **2002**, *74*, 703–740.
 53. Schnadt, J.; Brühwiler, P. A.; Patthey, L.; O'Shea, J. N.; Södergren, S.; Odelius, M.; Ahuja, R.; Karis, O.; Bässler, M.; Persson, P.; et al. Experimental Evidence for Sub-3-fs Charge Transfer from an Aromatic Adsorbate to a Semiconductor. *Nature* **2002**, *418*, 620–623.
 54. de Jong, M. P.; Friedlein, R.; Sorensen, S. L.; Öhrwall, G.; Osikowicz, W.; Tengsted, C. Orbital-Specific Dynamic Charge Transfer from Fe(II)-tetraphenylporphyrin Molecules to Molybdenum Disulfide Substrates. *Phys. Rev. B* **2005**, *72*, 035448.
 55. Föhlisch, A.; Feulner, P.; Hennies, F.; Fink, A.; Menzel, D.; Sanchez-Portal, D.; Echenique, P. M.; Wurth, W. Direct Observation of Electron Dynamics in the Attosecond Domain. *Nature* **2005**, *436*, 373–376.
 56. Neppel, S.; Bauer, U.; Menzel, D.; Feulner, P.; Shaporenko, A.; Zharnikov, M.; Kao, P.; Allara, D. Charge Transfer Dynamics in Self-Assembled Monomolecular Films. *Chem. Phys. Lett.* **2007**, *447*, 227–231.
 57. Kao, P.; Neppel, S.; Feulner, P.; Allara, D. L.; Zharnikov, M. Charge Transfer Time in Alkanethiolate Self-Assembled Monolayers via Resonant Auger Electron Spectroscopy. *J. Phys. Chem. C* **2010**, *114*, 13766–13773.
 58. Hamoudi, H.; Neppel, S.; Kao, P.; Schüpbach, B.; Feulner, P.; Terfort, A.; Allara, D.; Zharnikov, M. Orbital-Dependent Charge Transfer Dynamics in Conjugated Self-Assembled Monolayers. *Phys. Rev. Lett.* **2011**, *107*, 027804-1–027801-4.
 59. Blobner, F.; Coto, P. B.; Allegretti, F.; Bockstedte, M.; Rubio-Pons, O.; Wang, H.; Allara, D. L.; Zharnikov, M.; Thoss, M.; Feulner, P. Orbital Symmetry Dependent Electron Transfer through Molecules Assembled on Metal Substrates. *J. Phys. Chem. Lett.* **2012**, *3*, 436–440.
 60. Caprioli, F.; Decker, F. A New Simple Method To Heal Defects and To Improve Electrode Passivity of Aromatic SAMs on Gold. *J. Electroanal. Chem.* **2013**, *708*, 68–72.
 61. Ganesh, V.; Lakshminarayanan, V. Scanning Tunneling Microscopy, Fourier Transform Infrared Spectroscopy, and Electrochemical Characterization of 2-Naphthalenethiol Self-Assembled Monolayers on the Au Surface: A Study of Bridge-Mediated Electron Transfer in $\text{Ru}(\text{NH}_3)_6^{2+}/\text{Ru}(\text{NH}_3)_6^{3+}$ Redox Reactions. *J. Phys. Chem. B* **2005**, *109*, 16372–16381.
 62. Jiang, P.; Nion, A.; Marchenko, A.; Piot, L.; Fichou, D. Rotational Polymorphism in 2-Naphthalenethiol SAMs on Au(111). *J. Am. Chem. Soc.* **2006**, *128*, 12390–12391.
 63. Ballav, N.; Schüpbach, B.; Dethloff, O.; Feulner, P.; Terfort, A.; Zharnikov, M. Direct Probing Molecular Twist and Tilt in Aromatic Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2007**, *129*, 15416–15417.
 64. Ballav, N.; Schüpbach, B.; Neppel, S.; Feulner, P.; Terfort, A.; Zharnikov, M. Biphenylnitrile-Based Self-Assembled Monolayers on Au(111): Spectroscopic Characterization and Resonant Excitation of the Nitrile Tail Group. *J. Phys. Chem. C* **2010**, *114*, 12719–12727.
 65. Ponomarev, V. I.; Filipenko, O. S.; Atovmyan, L. O. Crystal and Molecular–Structure of Naphthalene at –150 Degrees Celsius. *Kristallografiya* **1976**, *21*, 392–394.
 66. Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y. T.; Parikh, A. N.; Nuzzo, R. G. Comparison of the Structures and Wetting Properties of Self-Assembled Monolayers of *N*-Alkanethiols on the Coinage Metal Surfaces, Cu, Ag, Au. *J. Am. Chem. Soc.* **1991**, *113*, 7152–7167.
 67. Zharnikov, M.; Grunze, M. Spectroscopic Characterization of Thiol-Derived Self-Assembled Monolayers. *J. Phys.: Condens. Matter* **2001**, *13*, 11333–11365.

68. Zharnikov, M. High-Resolution X-ray Photoelectron Spectroscopy in Studies of Self-Assembled Organic Monolayer. *J. Electron Spectrosc. Relat. Phenom.* **2010**, *178*, 179–380–393.
69. Hamoudi, H.; Kao, P.; Nefedov, A.; Allara, D. L.; Zharnikov, M. X-ray Spectroscopy Characterization of Self-Assembled Monolayers of Nitrile-Substituted Oligo(phenylene ethynylene)s with Variable Chain Length. *Beilstein J. Nanotechnol.* **2012**, *3*, 12–24.
70. Thome, J.; Himmelhaus, M.; Zharnikov, M.; Grunze, M. Increased Lateral Density in Alkanethiolate Films on Gold by Mercury Adsorption. *Langmuir* **1998**, *14*, 7435–7449.
71. Waske, P.; Wächter, T.; Terfort, A.; Zharnikov, M. Nitro-Substituted Aromatic Thiolate Self-Assembled Monolayers: Structural Properties and Electron Transfer upon Resonant Excitation of the Tail Group. *J. Phys. Chem. C* **2014**, *118*, 26049–26060.
72. Greenler, R. G. Infrared Study of Adsorbed Molecules on Metal Surfaces by Reflection Techniques. *J. Chem. Phys.* **1966**, *44*, 310–315.
73. Stöhr, J. *NEXAFS Spectroscopy*; Springer-Verlag: Berlin, 1992.
74. Horsley, J.; Stöhr, J.; Hitchcock, A. P.; Newbury, D. C.; Johnson, A. L.; Sette, F. Resonances in the K-Shell Excitation Spectra of Benzene and Pyridine: Gas Phase, Solid and Chemisorbed States. *J. Chem. Phys.* **1985**, *83*, 6099–6107.
75. Yokoyama, T.; Seki, K.; Morisada, I.; Edamatsu, K.; Ohta, T. X-ray Absorption Spectra of Poly-*p*-phenylenes and Polyacenes: Localization of π^* Orbitals. *Phys. Scr.* **1990**, *41*, 189–192.
76. Frey, S.; Stadler, V.; Heister, K.; Eck, W.; Zharnikov, M.; Grunze, M.; Zeysing, B.; Terfort, A. Structure of Thioaromatic Self-Assembled Monolayers on Gold and Silver. *Langmuir* **2001**, *17*, 2408–2415.
77. Robin, M. B.; Ishii, I.; McLaren, R.; Hitchcock, A. P. Fluorination Effects on the Inner-Shell Spectra of Unsaturated Molecules. *J. Electron Spectrosc. Relat. Phenom.* **1988**, *47*, 53–92.
78. Ågren, H.; Vahtras, O.; Carravetta, V. Near-Edge Core Photoabsorption in Polyacenes: Model Molecules for Graphite. *Chem. Phys.* **1995**, *196*, 47–58.
79. Oji, H.; Mitsumoto, R.; Ito, E.; Ishii, H.; Ouchi, Y.; Seki, K.; Yokoyama, T.; Ohta, T.; Kosugi, N. Core Hole Effect in NEXAFS Spectroscopy of Polycyclic Aromatic Hydrocarbons: Benzene, Chrysene, Perylene, and Coronene. *J. Chem. Phys.* **1998**, *109*, 10409–10418.
80. Dauselt, J.; Zhao, J.; Kind, M.; Binder, R.; Bashir, A.; Terfort, A.; Zharnikov, M. Compensation of the Odd–Even Effects in Aliphatic Self-Assembled Monolayers by Non-symmetric Attachment of the Aromatic Part. *J. Phys. Chem. C* **2011**, *115*, 2841–2854.
81. Rangan, S.; Gallet, J.-J.; Bournel, F.; Kubsky, S.; Le Guen, K.; Dufour, G.; Rochet, F.; Sirotti, F.; Carniato, S.; Ilakovac, V. Adsorption of Benzonitrile on Si(001)– 2×1 at 300 K. *Phys. Rev. B* **2005**, *71*, 165318–1–165318–12.
82. Carniato, S.; Ilakovac, V.; Gallet, J.-J.; Kuk, E.; Luo, Y. Hybrid Density-Functional Theory Calculations of Near-Edge X-ray Absorption Fine-Structure Spectra: Applications on Benzonitrile in Gas Phase. *Phys. Rev. A* **2005**, *71*, 022511.
83. Hautman, J.; Bareman, J. P.; Mar, W.; Klein, M. L. Molecular Dynamics Investigations of Self-Assembled Monolayers. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2031–2037.
84. Frey, S.; Shaporenko, A.; Zharnikov, M.; Harder, P.; Allara, D. L. Self-Assembled Monolayers of Nitrile-Functionalized Alkanethiols on Gold and Silver Substrates. *J. Phys. Chem. B* **2003**, *107*, 7716–7725.
85. Cassie, A. B. D.; Baxter, S. Wettability of Porous Surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546–551.
86. Ossowski, J.; Rysz, J.; Krawiec, M.; Maciazek, D.; Postawa, Z.; Terfort, A.; Cyganik, P. Oscillations in the Stability of Chemical Bonds Revealed by Ion-Induced Desorption. *Angew. Chem., Int. Ed.* **2015**, *54*, 1336–1340.
87. Piancastelli, M. N. Auger Resonant Raman Studies of Atoms and Molecules. *J. Electron Spectrosc. Relat. Phenom.* **2000**, *107*, 1–26.
88. Kempgens, B.; Kivimäki, A.; Neeb, M.; Köppe, H. M.; Bradshaw, A. M.; Feldhaus, J. A High-Resolution N 1s Photoionization Study of the N₂ Molecule in the Near-Threshold Region. *J. Phys. B* **1996**, *29*, 5389–5403.
89. Wurth, W.; Föhlisch, A. *Direct Observation of Electron Dynamics at Surfaces Using X-ray Spectroscopy*; Ultrafast Phenomena XV. Springer Series in Chemical Physics; Springer-Verlag: Berlin, 2007; Vol. 88, pp 707–709.
90. Wyczawska, S.; Cyganik, P.; Terfort, A.; Lievens, P. Ion-Beam-Induced Desorption as a Method for Probing the Stability of the Molecule–Substrate Interface in Self-Assembled Monolayers. *ChemPhysChem* **2011**, *12*, 2554–2557.
91. Konopka, M.; Rousseau, R.; Stich, I.; Marx, D. Detaching Thiolates from Copper and Gold Clusters: Which Bonds To Break? *J. Am. Chem. Soc.* **2004**, *126*, 12103–12111.
92. Konopka, M.; Rousseau, R.; Stich, I.; Marx, D. Electronic Origin of Disorder and Diffusion at a Molecule–Metal Interface: Self-Assembled Monolayers of CH₃S on Cu(111). *Phys. Rev. Lett.* **2005**, *95*, 096102.
93. Liao, K.-C.; Yoon, H. J.; Bowers, C. M.; Simeone, F. C.; Whitesides, G. M. Replacing Ag¹⁵⁵CH₃-R with Ag¹⁰⁷O₂-C-R in EGaIn-Based Tunneling Junctions Does Not Significantly Change Rates of Charge Transport. *Angew. Chem., Int. Ed.* **2014**, *53*, 3889–3893.
94. Bowers, C. M.; Liao, K.-C.; Zaba, T.; Rappoport, D.; Baghbanzadeh, M.; Breiten, B.; Krzykawska, A.; Cyganik, P.; Whitesides, G. M. Characterizing the Metal–SAM Interface in Tunneling Junctions. *ACS Nano* **2015**, *9*, 1471–1477.
95. Allan, M.; Chamon, S.; Hu, Q.-Y.; Imase, H.; Papillon, J. Arylpyridine Derivatives as Aldosterone Synthase Inhibitors. Patent WO 2011/061168, 2011.
96. Grenader, K.; Schüpbach, B.; Peters, A.; Kümmel, O.; Halter, O.; Terfort, A. Catalytic C–Se Bond Formation under Very Mild Conditions for the Two-Step, One-Pot Synthesis of Arylselenoacetates. *Adv. Synth. Catal.* **2012**, *354*, 2653–2658.
97. Grenader, K.; Kind, M.; Silies, L.; Peters, A.; Bats, J. W.; Bolte, M.; Terfort, A. Structural Characterization of a Series of Aryl Selenoacetates. *J. Mol. Struct.* **2013**, *1039*, 61–70.
98. Rane, A. M.; Miranda, E. I.; Soderquist, J. A. Potassium Triisopropylsilylthiolate: Vinyl and Aryl Sulfides through Pd Catalyzed Cross Coupling. *Tetrahedron Lett.* **1994**, *35*, 3225–3226.
99. Fernandez-Rodriguez, M. A.; Shen, Q. L.; Hartwig, J. F. A General and Long-Lived Catalyst for the Palladium-Catalyzed Coupling of Aryl Halides with Thiols. *J. Am. Chem. Soc.* **2006**, *128*, 2180–2181.
100. Hartwig, J. F. Evolution of a Fourth Generation Catalyst for the Amination and Thioetherification of Aryl Halides. *Acc. Chem. Res.* **2008**, *41*, 1534–1544.
101. Fernandez-Rodriguez, M. A.; Hartwig, J. F. A General and Long-Lived Catalyst for the Palladium-Catalyzed Coupling of Aryl Halides with Thiols. *Chem.—Eur. J.* **2010**, *16*, 2355–2359.
102. Satterley, C. J.; Lovelock, K. R. J.; Thom, I.; Dhanak, V. R.; Buck, M.; Jones, R. G. Normal Incidence X-ray Standing Wave Analysis of Thin Gold Films. *Surf. Sci.* **2006**, *600*, 4825–4828.
103. Heister, K.; Zharnikov, M.; Grunze, M.; Johansson, L. S. O.; Ulman, A. Characterization of X-ray Induced Damage in Alkanethiolate Monolayers by High-Resolution Photoelectron Spectroscopy. *Langmuir* **2001**, *17*, 8–11.
104. Moulder, J. F.; Stickle, W. E.; Sobol, P. E.; Bomben, K. D. In *Handbook of X-ray Photoelectron Spectroscopy*; Chastian, J., Ed.; Perkin-Elmer Corp.: Eden Prairie, MN, 1992.
105. Batson, P. E. Carbon-1s Near-Edge-Absorption Fine-Structure in Graphite. *Phys. Rev. B* **1993**, *48*, 2608–2610.
106. Domke, M.; Mandel, T.; Puschmann, A.; Xue, C.; Shirley, D. A.; Kaindl, G.; Petersen, H.; Kuske, P. Performance of the

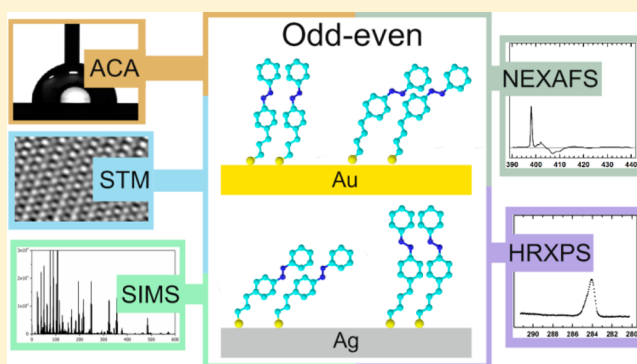
- High-Resolution SX700/II Monochromator. *Rev. Sci. Instrum.* **1992**, *63*, 80–89.
107. Cyganik, P.; Vandeweert, E.; Postawa, Z.; Bastiaansen, J.; Vervaecke, F.; Lievens, P.; Silverans, R. E.; Winograd, N. Modification and Stability of Aromatic Self-Assembled Monolayers upon Irradiation with Energetic Particles. *J. Phys. Chem. B* **2005**, *109*, 5085–5094.

Odd–Even Effects in the Structure and Stability of Azobenzene-Substituted Alkanethiolates on Au(111) and Ag(111) Substrates

Dominika Gnatek,[†] Swen Schuster,[‡] Jakub Ossowski,[†] Musammir Khan,[‡] Jakub Rysz,[†] Simone Krakert,[§] Andreas Terfort,[§] Michael Zharnikov,^{*,‡} and Piotr Cyganik^{*,†}[†]Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Krakow, Poland[‡]Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany[§]Institut für Anorganische und Analytische Chemie, Universität Frankfurt, Max-von-Laue-Strasse 7, 60438 Frankfurt, Germany

S Supporting Information

ABSTRACT: Structural properties and stability of the self-assembled monolayers (SAMs) of two prototypical azobenzene-based alkanethiols ($\text{C}_6\text{H}_5\text{--N=N--C}_6\text{H}_4\text{--(CH}_2\text{)}_n\text{--SH}$) on Au(111) and Ag(111) substrates were studied in detail using a combination of complementary experimental techniques. The azobenzene moiety in these films was linked to the thiol headgroup via short aliphatic spacers of variable length, i.e., $(\text{CH}_2)_3$ or $(\text{CH}_2)_4$, corresponding to a different parity of n . For both Au(111) and Ag(111) substrates, a pronounced dependence of the packing density and molecular inclination on the parity of n was observed, with a higher packing density (by $\sim 14\%$) and smaller inclination (by $\sim 17^\circ$) of the azobenzene moieties for $n = \text{odd}$ as compared to $n = \text{even}$ on Au(111) and reversed, but somewhat reduced, behavior on Ag(111). This dependence was related to the well-known odd–even effects in molecular assembly on noble metal substrates, reported previously for a variety of oligophenyl-substituted alkanethiolate SAMs and observed now for the azobenzene-substituted monolayers as well, underlining their generality. The structural odd–even behavior was accompanied by odd–even effects in the stability of the substrate–S bond, with the latter effects being directly correlated to the respective structure variation. The above results are of general importance for the design of functional monomolecular films and of a particular significance as a basis for dedicated photoisomerization experiments.



1. INTRODUCTION

Design and functionalization of thin organic films play a key role in many nanotechnological applications, with thiol self-assembled monolayers (SAMs)^{1,2} on metal substrate being one of the basic prototypical systems offering well-defined, highly ordered, and relatively stable monomolecular films. Despite conceptual simplicity and easiness of formation the correlation between structure, stability, and specific functionality of SAMs is still not completely clarified. This information is particularly scarce for less intensively investigated molecules with aromatic backbone which are of potential interest for both basic research and specific applications such as molecular electronics, lithography, nanofabrication, etc.^{3–7} For purely aromatic thiol-based SAMs, a high concentration of structural defects was observed as a result of surface stress induced by the misfit between the lattice preferred by the aromatic moieties and the one favored by the metal substrate.^{8,9} However, dedicated studies demonstrated that introduction of a more flexible aliphatic chain, as a spacer between the rigid aromatic moiety and the anchoring thiol group, can at least partly solve this problem, giving additional degrees of freedom and, thus, providing suitable pathways to reduce the stress without

distorting the film structure.¹⁰ The insertion of an aliphatic spacer, $(\text{CH}_2)_n$, the length of which is described by the parameter n , has pronounced consequences for the resulting SAM structures. As demonstrated by detailed microscopic and spectroscopic studies for the homologous series of biphenyl- and terphenyl-substituted alkanethiols^{11–20} and alkanesele-nols^{21–23} on the Au(111) and the Ag(111) substrates the structure of these SAMs depends strongly on the parity of n . In particular, on the Au(111) substrate, higher density structures of more upright-oriented molecules are formed by the odd-numbered homologues, in contrast to the even-numbered molecules exhibiting the opposite behavior. Interestingly, this “odd–even” effect is reversed on Ag(111) substrates, resulting in higher packing density structures of more upright-oriented molecules for the even-numbered homologues and vice versa. Significantly, the odd–even effect not only involves a structural modification of the araliphatic SAMs but also, as documented by the comparison studies for biphenyl-substituted alkanethiols

Received: August 13, 2015

Revised: October 16, 2015

Published: October 20, 2015

and -selenols on Au(111), has deep consequences for other film properties, such as their stability toward electrochemical desorption,^{24,25} ion-induced desorption,²⁶ electron irradiation,²⁷ exchange by alternative SAM precursors,^{28,29} and thermally induced phase transitions.^{30–33} We would like to note at this point that odd–even effects are a general phenomenon, occurring also in pure aliphatic SAMs.³⁴ Interestingly, recent experiments demonstrate that the odd–even effect can also be used to control tunneling rates in molecular junctions.^{35–39}

In the present study we test to what extent the concept of the odd–even effects is applicable to the aliphatic SAMs with azobenzene substitution, which, in the trans state, has a planar conformation, analogous to oligophenyl units in densely packed molecular films.⁴⁰ Note that this functional moiety is of particular importance in view of its well-known photochromic behavior,^{3,41} i.e., light-induced trans–cis and cis–trans conformational changes, attractive in context of stimuli-responsive systems and potential applications in molecular electronics,⁴² as active recognition systems,⁴³ etc., as far as azobenzene-bearing molecules can be assembled on a solid substrate in a suitable fashion. Along these lines, a variety of different azobenzene-based thiolate SAMs were studied, including purely aromatic monolayers based on biphenyl azobenzene,^{42,44–49} hybrid aliphatic–aromatic films,^{50–53} as well as mixed SAMs comprised of azobenzene-functionalized molecules and short “matrix” moieties.^{54–57} The reason for the use of such mixed SAMs with the functional molecules “diluted” by the matrix species is to release possible steric hindrances imposed by the neighbor molecules in the densely packed films, limiting the sterically demanding trans–cis conformation change of the azobenzene units. Such steric hindrances are believed to be the major constraint preventing the fabrication of reliable, stimuli-responsive, azobenzene-based monolayers,⁴⁴ along with the quenching of the preisomerization excited state by interaction with the substrate⁵⁸ and excitonic coupling among the azobenzene chromophores,⁵⁹ discussed also in this context. However, it has been demonstrated that for certain SAMs, like those with the rigid aromatic backbone with embedded azobenzene moiety, quite effective isomerization is possible even for well-ordered and densely packed structure, due to a cooperative character of the switching process occurring, presumably in a domino-like fashion.^{42,44–48,35} Such strategy, relying on cooperative switching in well-ordered, densely packed films rather than that of isolated azobenzene-bearing molecules, implanted in an inert matrix, should be potentially more efficient. The question is whether the observed cooperative isomerization behavior is a broad phenomenon for ordered molecular films or rather an exception, characteristic of specific molecular arrangements in few selected cases only.

In contrast to the SAMs based on rigid, oligophenyl backbone with embedded azobenzene moiety,^{44,49} the structural order of monolayers, in which this moiety is linked to the thiol group via an aliphatic chain,^{51,60} is usually much lower. In particular, this lack of structural order is associated with much smaller changes in the work function upon the isomerization of such SAMs⁵⁰ as compared to those with the oligophenyl backbone.⁴⁵ Significantly, lower structural quality of SAMs where an aliphatic chain is used to link the azobenzene moiety and the anchoring thiol group seems to be inconsistent with the reported earlier general improvement^{12–18,21–23,25–33} of the structure quality of aromatic SAMs upon insertion of the more

flexible aliphatic chain as a spacer between rigid aromatic structure and the substrate. However, there are two important aspects which question this seeming impression. First, the alkyl chains were not linked to the aromatic moiety directly, as was the case in the previous studies with the biphenyl or terphenyl substitutions,^{9–17,19–27} but via either ether^{50–52,54–57} or amide^{51,53,60} groups which typically distort the all-trans conformation⁶¹ essential for the odd–even effects.^{18,22} Second, in most cases, the alkyl linker was quite long in the context of our analysis (e.g., $n = 12$),⁵⁵ which potentially diminishes the positive effect of the alkyl linker at a proper n .²² Therefore, in the present study, we eliminate the above limitations and investigate the structure of SAMs where the alkyl linker is short enough ($n = 3$ or 4) and directly attached to the azobenzene moiety (see Figure 1). By performing structural analysis and

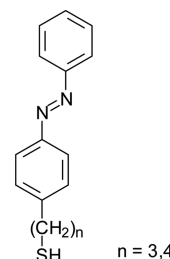


Figure 1. Molecules used in this study. Azo-3 and Azo-4 acronyms correspond to $n = 3$ and 4, respectively; Azo- n will be used as a joint abbreviation for both molecules.

stability tests for these SAMs on the Au(111) and the Ag(111) substrates, we demonstrate the applicability of the odd–even effect concept to azobenzene-substituted monolayers, with a particular emphasis on the possibility to form highly ordered molecular films.

2. EXPERIMENTAL METHODS

2.1. SAM Preparation. The Azo- n compounds were synthesized according to the protocols laid out in the literature.⁶¹ The substrates were purchased from Georg Albert PVD, Germany. They were prepared by thermal evaporation of 100 nm of gold or silver (99.99% purity) onto mica or polished single-crystalline silicon (100) wafers (Silicon Sense) primed with a 5 nm titanium adhesion layer. The mica substrates were preliminarily annealed at 320 °C for 24 h prior to the metal evaporation, done at the same temperature. The evaporated films were polycrystalline, with a grain size of 20–50 nm for Si or a terrace size of 100–200 nm for mica. Both grains and terraces predominantly exhibit a (111) orientation.^{62,63} The SAMs were formed by immersion of freshly prepared substrates into 1 mmol of solutions of Azo- n in absolute ethanol for 24 h at either room (21 °C) or elevated (60 °C) temperature, denoted as RT and ET below. After immersion, the samples were carefully rinsed with pure ethanol, blown dry with argon, and kept, in the case of the experiments at the synchrotron (see below), for several days in argon-filled glass containers until characterization. No evidence for impurities or oxidative degradation products was found.

2.2. Characterization. The Azo- n SAMs were characterized by scanning tunneling microscopy (STM), high-resolution X-ray photoelectron spectroscopy (HRXPS), angle-resolved near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and secondary ion mass spectroscopy (SIMS) and subjected to

dedicated exchange experiments. All spectroscopic (HPXPS, NEXAFS) and stability (SIMS, dedicated exchange) experiments were performed on the samples prepared at 60 °C, because of their superior structural ordering (see *STM Analysis* below).

2.3. STM. The STM measurements were performed for the Au(111) substrate only. In our experience, the quality of the STM images for SAMs on silver is inferior to those for gold,^{64,65} so that we refrained from any STM experiments for the films on Ag(111). For the STM measurements, only the gold films on mica were used. The Au substrates were flame annealed in a butane–oxygen flame prior to SAM preparation. The experiments were carried out in air at room temperature using a DI Nanoscope IIIa microscope. In all cases tips were prepared mechanically by cutting a 0.25 mm Pt/Ir alloy (8:2, Goodfellow) wire. Data were collected in constant current mode using a tunnelling current of 20–30 pA and a sample bias between 350 mV and 750 mV (sample positive).

2.4. HRXPS and NEXAFS Spectroscopy. The HRXPS and NEXAFS spectroscopy experiments were performed at the bending magnet beamline D1011 (bending magnet) at the MAX II storage ring at the MAX-IV laboratory in Lund, Sweden. The experiments were carried out under UHV conditions at a base pressure $< 1.5 \times 10^{-10}$ mbar. Special care, including a limited exposure of a particular spot as well as control measurements on reference samples, was taken to avoid potential damage induced by the primary X-rays.⁶⁶

The HRXP spectra were collected with a SCIENTA SES200 spectrometer. The spectra were acquired in normal emission geometry at photon energies of 350 eV for the S 2p region, 350 and 580 eV for the C 1s range, and 580 eV for the N 1s region. In addition, Au 4f and Ag 3d spectra were measured, and the O 1s range was monitored. The binding energy (BE) scale of every spectrum was individually calibrated using the Au 4f_{7/2} emission line of alkanethiolate-covered Au substrate at 84.0 eV.⁶⁷ The energy resolution was better than 100 meV, which is noticeably smaller than the full widths at half-maximum (fwhm) of the photoemission peaks addressed in this study. The accuracy of the BE/fwhm values is 0.02–0.03 eV. They were determined within a fitting procedure (symmetric Voigt functions and either a Shirley-type or linear background), along with the intensities of the emission peaks.

The latter values were used to derive the effective thickness of the Azo-*n* monolayers. The thickness was determined on the basis of either C 1s/Au 4f or C 1s/Ag 3d intensity ratios,⁶⁸ assuming a standard exponential attenuation of the photoelectron signal⁶⁹ and using the attenuation lengths typical of monomolecular films.⁷⁰ The spectrometer specific constants were determined using dodecanethiolate (DDT) and hexadecanethiolate (HDT) SAMs of well-known thicknesses as references.

The acquisition of the NEXAFS spectra was carried out at the carbon and nitrogen K-edges in the partial electron yield mode with retarding voltages of –150 and –300 V, respectively. Linear polarized synchrotron light with a polarization factor of ~95% was used. The energy resolution was better than 100 meV. The incidence angle of the X-ray light was varied from 90° (E vector in the surface plane) to 20° (E vector nearly normal to the surface) in steps of 10–20° to monitor the orientational order of the Azo-*n* molecules within the films. This approach is based on the linear dichroism in X-ray absorption, i.e., the strong dependence of the cross-section of the resonant photoexcitation process on the orientation of the

electric field vector of the linearly polarized light with respect to the molecular orbital of interest.⁷¹

The raw NEXAFS spectra were normalized to the incident photon flux by division through a spectrum of a clean, freshly sputtered gold sample, which was considered as the transmission of the beamline. In the case of Ag substrate, a spectrum of clean silver was subtracted from the raw spectrum of a SAM sample before normalization to correct for the difference in the electron yield between Ag and Au. Further, the spectra were reduced to the standard form by subtracting linear pre-edge background and normalizing to the unity edge jump (determined by a nearly horizontal plateau 40–50 eV above the respective absorption edges). The energy scale was referenced to the pronounced π_1^* resonance of highly oriented pyrolytic graphite (HOPG) at 285.38 eV⁷² in combination with the well-known $\Delta h\nu \propto (h\nu)^{3/2}$ behavior of plane grating monochromators.⁷³ The accuracy of the resultant energy positions are expected to be ± 0.05 eV.

The spectroscopic experiments were repeated several times on the individually prepared Azo-*n* SAMs with similar results. These experiments included additional XPS and NEXAFS measurements which were performed at the HE-SGM beamline of the synchrotron storage ring BESSY II in Berlin, Germany. The parameters of the beamline and experimental station can be found elsewhere.⁷⁴ A similar procedure as at the MAX-IV laboratory in Lund, Sweden, was applied.

2.5. Exchange Experiments. The relative stability of the Azo-3 and Azo-4 monolayers on Au(111) and Ag(111) substrates was probed by dedicated exchange experiments. The exchange process was performed by immersion of freshly prepared samples in the 1 mM ethanolic solution of 16-mercaptohexadecanoic acid, HS-(CH₂)₁₅-COOH (MHDA), at room temperature. The progress of the exchange reaction was monitored by consecutive measurements of the advancing water contact angle. The measurements were carried out with a Rame-Hart goniometer, model 200, using ultrapure water (~18 MΩ). The experiments were performed under ambient conditions (temperature = 21 °C, humidity = 25%) with the needle tip in contact with the drop. Averaged values of at least 100 measurements at a few different locations on each sample are reported.

2.6. SIMS. The SIMS experiments were performed using a TOF SIMS V system (ION TOF GmbH, Germany) operated at a base pressure of 5×10^{-10} mbar. The primary ion beam (30 keV Bi⁺) was scanned over a 500 μm × 500 μm area during data acquisition. All data were acquired under static SIMS (S-SIMS) conditions using a total ion dose of up to 7×10^{10} ions/cm², which, for this kind of SAMs, ensures analysis with negligible ion-induced damage.⁷⁵ The secondary ions were extracted into a reflectron time-of-flight mass spectrometer before reaching the MCP detector. For each type of the SAM, three different areas on three different samples were examined with a reproducibility of ~10% in the peak intensities. Before analysis all spectra were normalized to the respective total counts number.

3. RESULTS

3.1. Microscopic Analysis (STM). STM data obtained for Azo-3/Au(111) are presented in *Figure 2*. The overall morphology of the samples prepared at RT and ET is shown in *Figure 2a* and *2b*, respectively. The comparison of both images (obtained at the same scale) indicates a substantial increase of the average size of structural domains from ca. 5–10

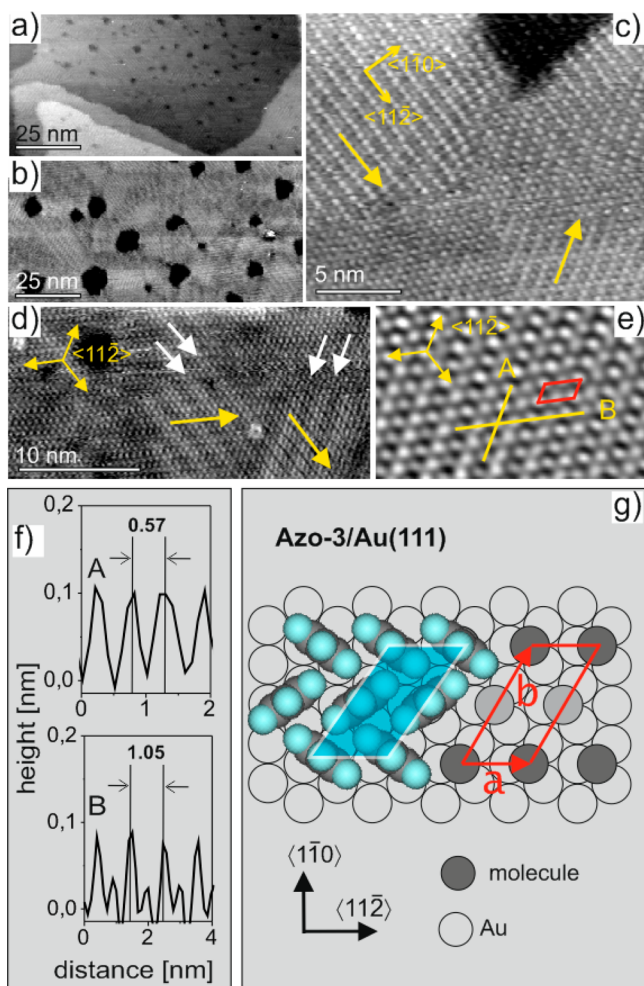


Figure 2. STM data for Azo-3/Au(111). STM images at different scale for the SAMs prepared at room temperature (a) and 60 °C (b–e). Yellow arrows in c and d mark the orientation of the rotational domains. White arrows in d indicate location and direction of bright bands (see text for details). The red parallelogram in e marks the oblique ($2\sqrt{3} \times 1.14\sqrt{3}$)R30° unit cell schematically presented in g together with the corresponding herringbone arrangement of the azobenzene moieties. Heights profiles A and B presented in f are taken along the yellow lines depicted in e.

nm for the RT preparation to ca. 30–50 nm for the ET incubation. Considering the higher structural order of the samples prepared at ET as compared to the RT procedure, all further STM analysis was performed for the former case. A representative high-resolution image presented in Figure 2c exhibits well-defined molecular structure with a characteristic stripe pattern of individual domains, strictly following the $11\bar{2}$ high-symmetry directions of the underlying Au(111) substrate. An STM image obtained at an intermediate scale (Figure 2d) reveals that this stripe pattern exhibits additional STM contrast variation in the form of much less regular and wider bright bands (indicated by the white arrows) appearing at a fixed angle of 60° with respect to each other (as marked by the yellow arrows), i.e., following other equivalent $11\bar{2}$ high-symmetry directions of the Au(111) substrate. A molecular resolved image shown in Figure 2e allows for identification of the oblique unit cell depicted in red. The characteristic dimensions of this cell, with $a = 0.57 \pm 0.03$ nm and $b = 1.05 \pm 0.05$ nm, are depicted in height profiles A and B taken in Figure 2f and

presented in Figure 2f. The respective unit cell can be described as an oblique ($2\sqrt{3} \times 1.14\sqrt{3}$)R30° structure which is slightly incommensurate with the Au(111) substrate along the a vector. With two molecules per unit cell, the molecular footprint for this structure amounts to 0.246 nm². A schematic cartoon with possible herringbone arrangement of the Azo-3 molecules in such a 2D lattice is shown in Figure 2g (for the sake of clarity, individual molecules are presented either as a phenyl ring or as a gray or black circle).

The analogous STM data collected for the Azo-4 monolayer are presented in Figure 3. As documented by the images shown

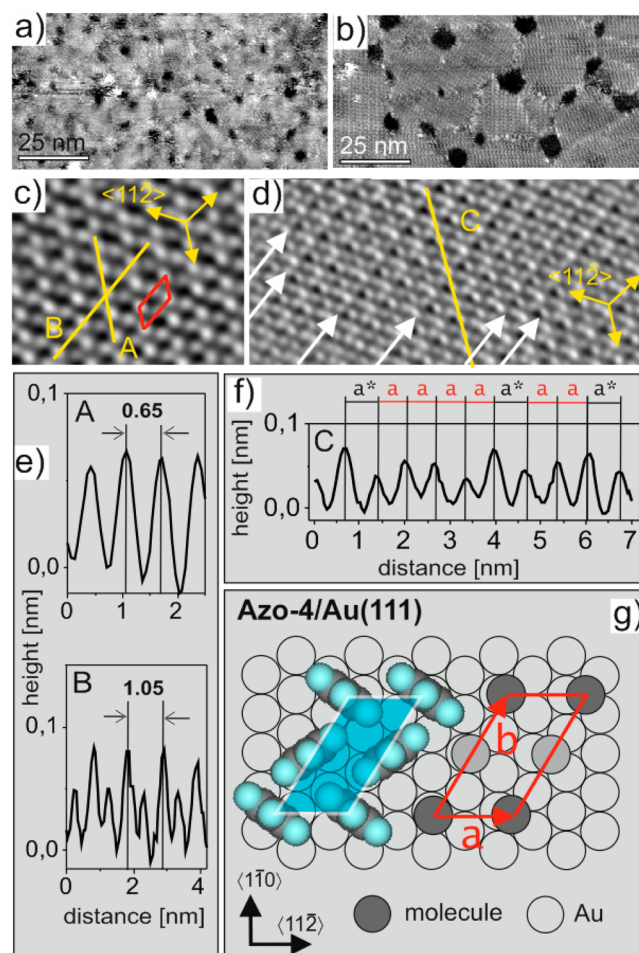


Figure 3. STM data for Azo-4/Au(111). STM images at different scale for the SAMs prepared at room temperature (a) and 60 °C (b–e). The red parallelogram in c marks the oblique ($2\sqrt{3} \times 1.3\sqrt{3}$)R30° unit cell schematically presented in g together with the corresponding herringbone arrangement of the azobenzene moieties. Heights profiles A and B presented in e are taken along the yellow lines depicted in c. The height profile C presented in f is taken along the yellow line depicted in d (see text for details). White arrows in d indicate location of line defects.

in Figure 3a and 3b, the preparation of Azo-4/Au(111) at 60 °C results in a larger size of rotational domains (30–50 nm) as compared to the RT procedure (5–10 nm), similarly to the Azo-3/Au(111) case. Molecularly resolved images obtained for Azo-4/Au(111) prepared at 60 °C (Figure 3c and 3d) reveal a similarly striped structure as that observed for the Azo-3 film, with a well-defined oblique unit cell marked in red in Figure 3c. The averaged dimensions of this unit cell, $a = 0.65 \pm 0.03$ nm

and $b = 1.05 \pm 0.05$ nm, calculated from the height profiles A and B marked in Figure 3c and presented in Figure 3e, are close to the oblique $(2\sqrt{3} \times 1.3\sqrt{3})R30^\circ$ structure which is incommensurate with the Au(111) substrate along the a unit cell vector. A larger size of this unit cell along the a vector, as compared to the $(2\sqrt{3} \times 1.14\sqrt{3})R30^\circ$ arrangement for Azo-3/Au(111), results in a molecular footprint of 0.281 nm^2 . The image presented in Figure 3d reveals an additional feature of the Azo-4/Au(111) structure, i.e., defect lines (indicated by the white arrows in Figure 3d) crossing the characteristic striped structure at a fixed angle of 60° , i.e., following another equivalent $11\bar{2}$ high-symmetry direction of the Au(111) substrate. The height profile C taken from the image in Figure 3d is presented in Figure 3f; this profile intersects the defect lines along the striped structure. Analysis of the profile shows that formation of the defect lines is not only associated with the modification of the apparent height of the molecules (which enables the identification) but, even more important, with the ca. 10% increase in the spacing between the molecules along the unit cell vector a, i.e., from 0.65 (indicated in Figure 3f by a) to 0.71 nm (indicated in this figure by a^*). A schematic cartoon illustrating a possible herringbone arrangement of the Azo-4 molecules in the incommensurate oblique $(2\sqrt{3} \times 1.30\sqrt{3})R30^\circ$ structure is shown in Figure 2g (for the sake of clarity, individual molecules are presented either as a phenyl ring or as a gray or black circle). We would like to point out that structural models for Azo-3(4) adsorption on the Au(111) surface are based on an unreconstructed Au(111) surface. Note that several different models of surface reconstruction upon thiol adsorption have been proposed so far for Au(111);^{76–80} however, in most cases, adsorption of ultimately short methanethiol molecules was considered. The intermolecular interactions were, thus, mostly neglected, in contrast to the case of much longer molecules investigated in our study. One can expect that a significant contribution of intermolecular interactions for Azo-3(4)/Au(111) SAMs to the overall energetics of the monolayer most probably influences the exact form of the Au(111) reconstruction^{81,82} to the point which remains unknown at the moment. Therefore, to indicate some basic correlations between the Au(111) substrate and the structure of the Azo-3(4) SAM, a simple unreconstructed surface was considered in the present analysis.

3.2. Spectroscopic Analysis (XPS and NEXAFS). The S 2p, C 1s, and N 1s HRXP spectra of Azo-3/Au(111) and Azo-4/Au(111) are presented in Figure 4. The S 2p spectra in Figure 4a exhibit a single S $2p_{3/2/1/2}$ doublet at 162.0 eV (S $2p_{3/2}$) commonly assigned to the thiolate moieties,^{66,83} with no traces of atomic sulfur, disulfide, unbound thiol, or oxidative species. This means that the molecules in the Azo-*n* films are attached to the Au(111) substrate via the thiolate anchor, corresponding to the typical SAM/Au(111) architecture. The C 1s spectra of Azo-*n*/Au(111) in Figure 4b exhibit a single, slightly asymmetric emission at a BE of 284.1–284.2 eV, with no trace of contamination such as CO or COOH. The emission stems predominantly from the azobenzene moiety since the C 1s signal from the short aliphatic linker is strongly attenuated at the given photon energy.⁸⁴ The asymmetry of the C 1s emission is most likely related to the electronegativity of the azo bridge nitrogen affecting the adjacent carbon atoms, which results in the appearance of a shoulder at the high BE side of the main peak.⁸⁵ A superposition of the main peak and the shoulder results then in an appearance of the joint asymmetric peak. The N 1s spectra of Azo-*n*/Au(111) in Figure 4c exhibit a

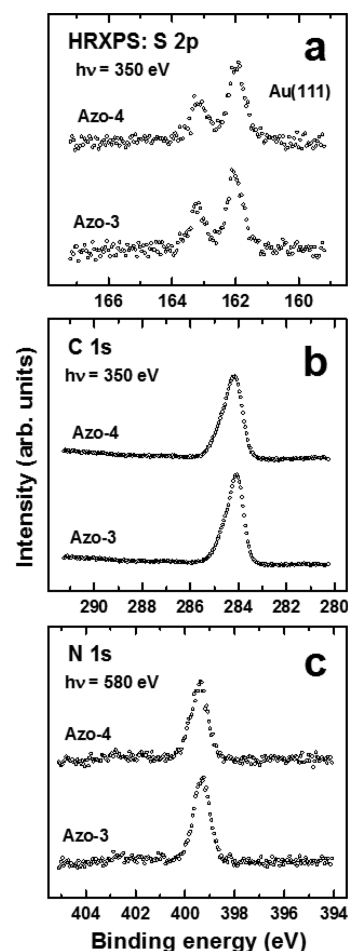


Figure 4. S 2p (a), C 1s (b), and N 1s (c) HRXP spectra of Azo-3/Au and Azo-4/Au. Photon energies are given in the panels.

single, symmetric emission at a BE of 399.3–399.4 eV, assigned to the nitrogen atoms of the azobenzene moiety.^{53,85}

The intensities of both C 1s and N 1s signals for Azo-3/Au(111) are somewhat higher than the respective intensities for Azo-4/Au(111), which suggest, in agreement with the STM data (see previous section), higher packing density for the former monolayer. Accordingly, a fingerprint of the packing density—effective thickness—was found to be 1.5 and 1.3 nm for Azo-3/Au(111) and Azo-4/Au(111), respectively, with the former value being noticeably higher than the latter in spite of the smaller molecular length of Azo-3 (1.46 nm) compared to Azo-4 (1.58 nm). On the basis of the above values, the difference in the packing density between the Azo-3/Au and the Azo-4/Au films on Au(111) could be estimated at ca. 14–15%, which is in excellent agreement with the STM-derived value ($\sim 14\%$).

Note that apart from the packing density difference, the effective thickness values for the Azo-3 and Azo-4 films on Au(111) are more or less close to the respective molecular lengths plus the length of the S–Au bond (0.24 nm),^{86,87} assuming an upright molecular orientation in both monolayers. The difference between the thickness and the molecular length is larger for Azo-4/Au(111) as compared to Azo-3/Au(111), suggesting a larger molecular inclination.

C and N K-edge NEXAFS spectra of the Azo-*n* films on Au(111) are presented in Figures 5 and 6, respectively. In Figures 5a and 6a, the spectra acquired at the so-called magic

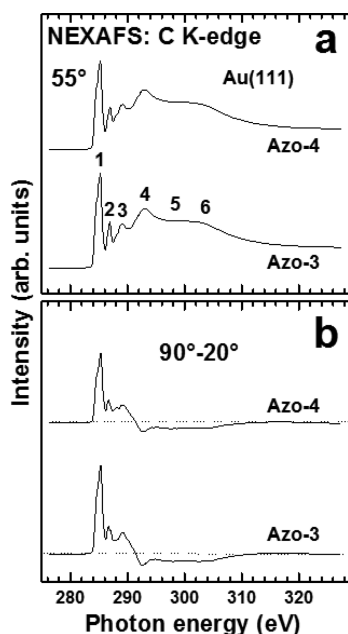


Figure 5. C K-edge NEXAFS spectra of Azo-3/Au and Azo-4/Au acquired at an X-ray incident angle of 55° (a), along with the respective difference between the spectra collected under the normal (90°) and grazing (20°) incidence geometry (b). Individual resonances are marked by numbers (see text for assignments). Horizontal dashed lines in b correspond to zero.

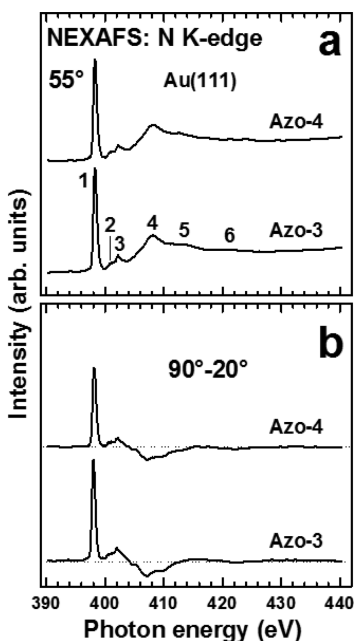


Figure 6. N K-edge NEXAFS spectra of Azo-3/Au and Azo-4/Au acquired at an X-ray incident angle of 55° (a), along with the respective difference between the spectra collected under the normal (90°) and grazing (20°) incidence geometry (b). Individual resonances are marked by numbers (see text for assignments). Horizontal dashed lines in b correspond to zero.

angle of X-ray incidence (55°) are shown; these spectra are not affected by any effects related to molecular orientation and are, therefore, exclusively representative of the chemical composition of the investigated samples.⁷¹ In Figures 5b and 6b, the differences between the spectra collected at X-ray incidence

angles of 90° and 20° are shown for both Azo-3/Au(111) and Azo-4/Au(111); such difference curves are a convenient way to monitor molecular orientation in organic films, relying on the linear dichroism effects in X-ray absorption (see section 2).⁷¹

The 55 °C K-edge spectra of the Azo-*n* films on Au(111) in Figure 5a exhibit an absorption edge related to the excitation of the C 1s electrons into the continuum states and the characteristic absorption resonances. The spectra are dominated by the pronounced, asymmetric π^* resonance of the azobenzene moiety at ~285.15 eV (1). Such an asymmetry is typical for azobenzene^{53,59,85,88} and related to a superposition of the C 1s to LUMO, LUMO+1, and LUMO+2 transitions merged in the joint resonance.^{88,89} This feature is accompanied by a Rydberg resonance (R^*) near 287.0 eV (2),^{53,85} a further π^* -like resonance of azobenzene at ~289.0 eV (3; C 1s $\rightarrow$ LUMO+4),⁸⁸ as well as several broad σ^* resonances at higher photon energies (4–6). Note that the resonance at 287.0 eV (2) can also be alternatively described as a π^* feature and assigned to the C 1s $\rightarrow$ LUMO+3 transition.⁸⁸ Note also that the resonances associated with the aliphatic linkers are hardly perceptible in the C K-edge spectra because of the small length of this unit and the attenuation of the respective signal by the azobenzene overlayer.

Characteristic absorption features of the azobenzene moiety were also observed at the N K-edge. The spectra of the Azo-*n* films in Figure 6a are dominated by a strong π^* resonance at ~398.3 eV (1) associated with the N 1s $\rightarrow$ LUMO transition.⁸⁸ This feature is accompanied by several weaker π^* resonances at ~400.9 (2) and 402.3 eV (3) corresponding to the N 1s $\rightarrow$ LUMO+3 (2) and N 1s $\rightarrow$ LUMO+4 (3) transitions⁸⁸ as well as by several broad π^* resonances at higher photon energies (4–6). In contrast, the N 1s $\rightarrow$ LUMO+1 and N 1s $\rightarrow$ LUMO+2 features are not observed at the N K-edge, which suggests that the respective orbitals are located mainly at the phenyl rings and not at the azo bridge.⁸⁹

Both C and N K-edge NEXAFS spectra of the Azo-*n* films on Au(111) exhibit pronounced linear dichroism as evidenced by the characteristic peaks at the positions of the absorption resonances in Figures 5a and 6a. This is a clear signature of orientational order. In addition, the positive sign of the observed difference peaks for the π^* resonances implies an upright orientation of the molecular constituents in the monolayers in view of the fact that the π^* orbitals are directed perpendicular to the molecular backbone. The opposite situation, with a negative sign of the difference peaks, occurs for the σ^* orbitals, directed along the molecular backbone, supporting the statement about upright molecular orientation, in good agreement with the HRXPS data (see previous section).

Along with the above qualitative considerations, a quantitative analysis of the entire set of C and N-K-edge NEXAFS spectra of the Azo-*n* films on Au(111) acquired at different angles of X-ray incidence was performed. For this analysis we used the most prominent π_1^* resonances at both edges and the standard theoretical framework for vector-type orbitals.^{71,90} The derived average tilt angles of the π^* orbitals representative mostly of the phenyl rings (from the C K-edge data) and exclusively of the N=N bridge (from the N K-edge data) are compiled in Table 1, together with some relevant STM and HRXPS results. There are two important findings related to the angle values. First, the average tilt angle of the ring orbitals is close to that of the N=N bridge for both Azo-3/Au and Azo-4/Au assuming a close-to-planar, trans

Table 1. Overview of the Parameters for the Azo-*n* Films on Au(111) and Ag(111)^a

system	molecular footprint (nm ²) (STM)	effective thickness (Å) (HRXPS)	tilt π_1^* phenyl (NEXAFS)	tilt π^* N=N (NEXAFS)	molecular tilt (NEXAFS)
Azo-3/Au	0.246	15.0	70.5°	75.7°	20°
Azo-4/Au	0.281	13.0	57°	60°	37°
Azo-3/Ag		12.9	63.5°	64.5°	31°
Azo-4/Ag		15.5	70.5°	70.5°	23°

^aMolecular lengths of Azo-3 and Azo-4 are 1.46 and 1.58 nm, respectively. The error of the angle values is $\pm 3^\circ$.

conformation for the majority of the molecules in the respective monolayers. Second, the tilt angles for the π^* orbitals of Azo-3/Au are noticeably larger than those for Azo-4/Au, suggesting a smaller molecular inclination in the former case, in full agreement with the HRXPS data.

The tilt angles for the π^* orbitals can be used to calculate the average tilt angles of the molecular backbones as far as the so-called twist angle γ ,^{16,91} describing the rotation of the backbone along the molecular axis in relation to the tilt direction, is known; see Figure 7 where a schematic drawing of the Azo-3 molecule is given, representative also for the Azo-4 case. The twist angle can only be measured directly or derived indirectly in selected situations^{86,88,91–93} but can be reasonably assumed to be close to that derived for similar azobenzene-substituted

monolayers, i.e., $\sim 32^\circ$.⁸⁸ Surprisingly, this value coincides practically with the analogous value for the bulk biphenyl (32°).⁹⁴

The average tilt angles of the azobenzene backbones in the Azo-*n* films on Au(111), calculated within the above assumption regarding the molecular twist, are compiled in Table 1. Accordingly, the molecular inclination in Azo-3/Au(111) ($\sim 20^\circ$) is noticeably smaller than that in Azo-4/Au(111) (37°), in full agreement with the smaller molecular footprint and larger effective thickness (see Table 1).

Analogous spectroscopic experiments were also performed for the Azo-*n* SAMs on Ag(111). The HRXPS and NEXAFS spectra of these films were very similar to the analogous spectra for the monolayers on Au (Figures 4–6), apart from the intensity relations (HRXPS) and linear dichroism behavior (NEXAFS spectroscopy). The most important (in context of the present study) spectroscopic data for Azo-*n*/Ag(111) are compiled in Figure 8. As seen in Figure 8a, where the C 1s HRXP spectra are presented, the intensity of the C 1s signal is noticeably higher for Azo-4/Ag(111) compared to Azo-3/Ag(111). The derived effective thicknesses, compiled in Table 1, are 1.55 and 1.29 nm, respectively. The difference between these values is too large to be explained by the presence of the additional methylene group in the alkyl linker of the Azo-4 molecule compared to the Azo-3 moiety. Consequently, the HRXPS data suggest a higher packing density in the former case than in the latter, which is an inverse behavior compared to the films on the Au(111) substrate (see Figure 4b and 4c as well as Table 1).

The difference NEXAFS spectra, at both the C and the N K-edge, in Figure 8a and 8b, respectively, exhibit a similar, inverse behavior compared to the films on the Au(111) substrate (see Figures 5b and 6b). Indeed, the amplitude of the difference peaks at the positions of the characteristic absorption resonances is higher for Azo-4/Ag(111) compared to Azo-3/Ag(111), suggesting smaller molecular inclination in the former case. The derived angles of the π_1^* orbitals are compiled in Table 1. Similar to the Au(111) case, the C-edge and N K-edge derived values are close to each other for both monolayers studied, suggesting a close-to-planar, trans conformation for the majority of the SAM constituents on Ag(111) as well. At the same time, in contrast to the films on Au(111), the tilt angle of the π_1^* orbitals in Azo-4/Ag(111) is larger than in Azo-3/Ag(111), suggesting, in view of the orientation of these orbitals, a smaller molecular inclination in the former case. Accordingly, the average molecular tilt angles in Azo-3/Ag(111) and Azo-4/Ag(111) were estimated at 31° and 23° , respectively (see Table 1), exhibiting the inverse behavior with respect to the parity of *n* as compared to the films on Au(111).

3.3. Stability Analysis (Exchange Experiments and S-SIMS). The results of the exchange experiments for the Azo-*n* SAMs on Au(111) and Ag(111) are presented in Figure 9. Figure 9a shows advancing water contact angle (WCA) values

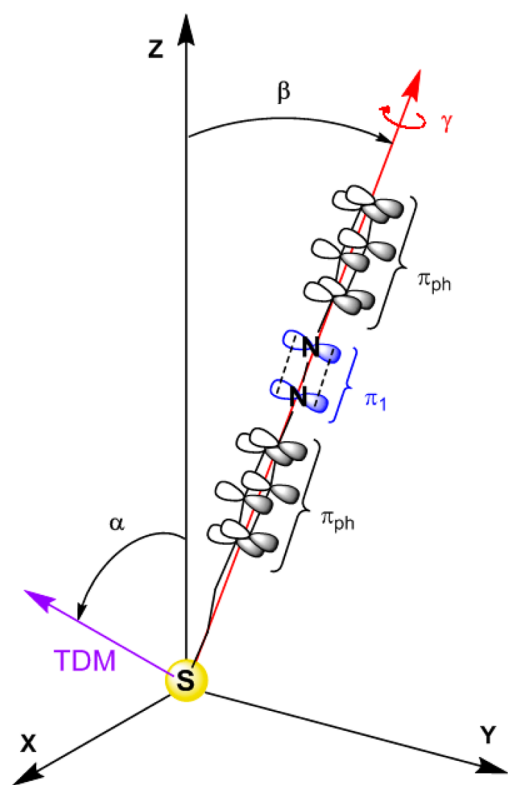


Figure 7. Schematic drawing of the orientation of the Azo-3 molecules in the trans conformation, representative also of Azo-4/Au. The phenyl rings and N=N bridge are considered to be coplanar, so that the π^* orbitals of the bridge (blue) are parallel to the π_{ph}^* orbitals of the rings (black). The backbone tilt angle β and twist angle γ describe the molecular orientation. The π^* orbitals are perpendicular to the molecular plane; the respective transition dipole moment TDM_π is shown as a violet arrow; its orientation is given by the angle α . At $\gamma = 0$, TDM_π lies in the plane spanned by the *z* axis and the axis of the azobenzene unit (red arrow). Angles are related by the equation, $\cos \alpha = \sin \beta \times \cos \gamma$ (see ref 14 for details).

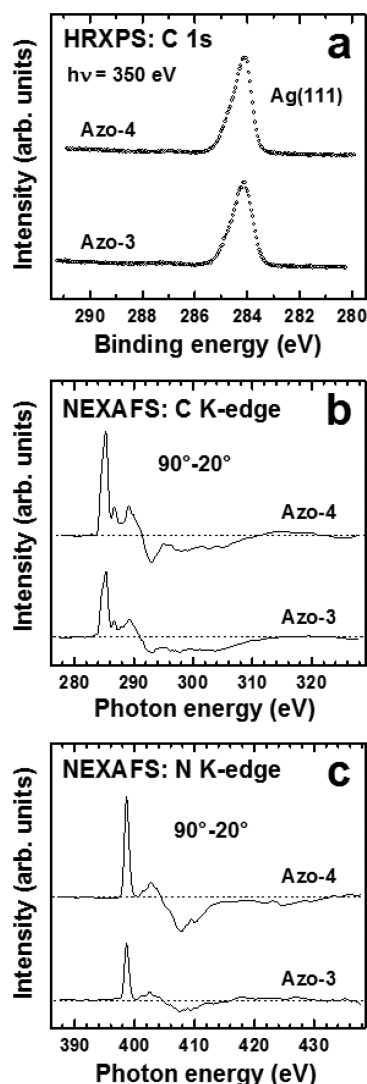


Figure 8. C 1s HRXP spectra (a) as well as the difference between the C K-edge (b) and the N K-edge (c) NEXAFS spectra collected under the normal (90°) and grazing (20°) incidence geometry for the Azo-*n* SAMs on Ag(111).

recorded for the Azo-3/Au(111) and Azo-4/Au(111) samples during their incubation in 1 mM ethanolic solution of the MHDA molecules terminated by the hydrophilic $-\text{COOH}$ group. For the pristine Azo-*n* films (i.e., at an incubation time of 0 h), the WCA value for Azo-3/Au(111) ($\sim 88^\circ$) is slightly higher than that for Azo-4/Au(111) ($\sim 85^\circ$), in agreement with previous reports.⁶¹ However, the analysis of the WCA values as a function of the incubation time in the MHDA solution shows drastic differences between Azo-3/Au(111) and Azo-4/Au(111). Whereas in the former case the WCA changed only slightly from an initial value of $\sim 88^\circ$ to $\sim 83^\circ$, after 22 h a much stronger decrease from an initial value of $\sim 85^\circ$ down to $\sim 70^\circ$ was observed for the latter case. On the basis of the above data, changes in the molecular composition were calculated according to the Cassie equation⁹⁵

$$\cos \theta_C = f_A \cos \theta_A + f_B \cos \theta_B; f_A + f_B = 1$$

which describes the effective contact angle value θ_C for a surface covered by fractions f_A and f_B of the materials A and B, the neat surfaces of which would expose contact angle values of θ_A and θ_B , respectively. The results of the calculations are presented in

Figure 9b as functions of the incubation time in the MHDA solution (the WCA value measured for the pristine MHDA SAMs on Au(111) and Ag(111) surface was $\sim 60^\circ$, similar to that reported in a previous study⁹⁶). As shown in this figure, there is about 20% exchange between the MHDA molecules in solution and the Azo-3 molecules in the SAM on Au(111) during the entire reaction time of 22 h. In contrast, for Azo-4/Au(111), an analogous analysis yields a much higher extent of exchange of about 65%. Analogous experiments have also been conducted for the Azo-*n* SAMs on Ag(111). The respective WCA data are presented in Figure 9c. For the pristine Azo-*n* films, the WCA values for both samples were quite similar, i.e., in the range of 95° , which is somewhat higher as compared to these monolayers on the Au(111) substrate. The analysis of the WCA as a function of the incubation time in the MHDA solution shows much smaller and reverse differences between the Azo-3 and the Azo-4 samples as compared to analogous measurements on the Au(111) substrate. An estimate of the extent of exchange during the entire incubation time (22 h) on the basis of the Cassie equation gives $\sim 57\%$ and $\sim 42\%$ in the case of Azo-3/Ag(111) and Azo-4/Ag(111), respectively (Figure 9d). Thus, Azo-3/Ag(111) is more stable with respect to the exchange reaction, exhibiting an inverse behavior as compared to the case of Au(111).

A second stability test was conducted by using the S-SIMS technique, which recently proved to be extremely useful in determination of the relative stability at the SAM–metal interface.^{93,97} Mass spectra of both negative and positive secondary ions for the Azo-*n* SAMs on Au(111) and Ag(111) are presented in Figures S1 and S2 in the Supporting Information. These spectra exhibit secondary ion signals typical of SAMs on metal substrate, i.e., sulfur–metal clusters (having the general form of $[\text{Au}_x\text{S}_y]^-$ or $[\text{Ag}_x\text{S}_y]^-$), different molecular fragments, and metal–molecule clusters (having the general form of $[\text{M}_x\text{Au}_y]^-$ or $[\text{M}_x\text{Ag}_y]^-$, with $\text{M} = \text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_4-(\text{CH}_2)_{3(4)}\text{S}$). We focused first on the positive secondary molecular ions related to the Azo-3 and Azo-4 molecules. Unfortunately, for both Au(111) and Ag(111) substrates, the signal corresponding to the complete molecular ion, $[\text{M}]^+ = [\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_4-(\text{CH}_2)_{3(4)}\text{S}]^+$, is very weak, so that a quantitative analysis was not possible. However, sufficiently high signals could be measured for positive ions associated with the desulfurized fragments ($[\text{M} - \text{S}]^+ = [\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-(\text{CH}_2)_{3(4)}]^+$) emitted as a result of the ion-impact-induced breaking of the S–C bond. The relative intensities of this particular ion for Azo-3/Au(111) and Azo-4/Au(111) are presented in Figure 10a, with ca. 65% higher signal in the former case. In contrast, for the Ag(111) substrate (Figure 10b), the emission of the $[\text{M} - \text{S}]^+$ ion from the Azo-3 film is ca. 30% lower as compared to the Azo-4 monolayer.

Similar odd–even effects were also visible in the emission of the secondary ions associated with the molecule–substrate clusters, in our case $[\text{M}_x\text{Au}_y]^-$ or $[\text{M}_x\text{Ag}_y]^-$. Emission of such clusters is known to be typical of SAMs on noble metal substrates.^{98–103} In the present case, a sufficiently strong signal was measured for the $[\text{M}_2\text{Au}(\text{Ag})]^-$ ions. As documented by the data shown in Figure 10c, the odd–even effect is particularly strong for the Au substrate where the $[\text{M}_2\text{Au}]^-$ signal measured for the Azo-4 SAM is only $\sim 20\%$ of the analogous signal measured for the Azo-3 monolayer. For Ag(111) (Figure 10d), the inverse behavior was observed: similar to the backbone ions analyzed above, a higher (by ca.

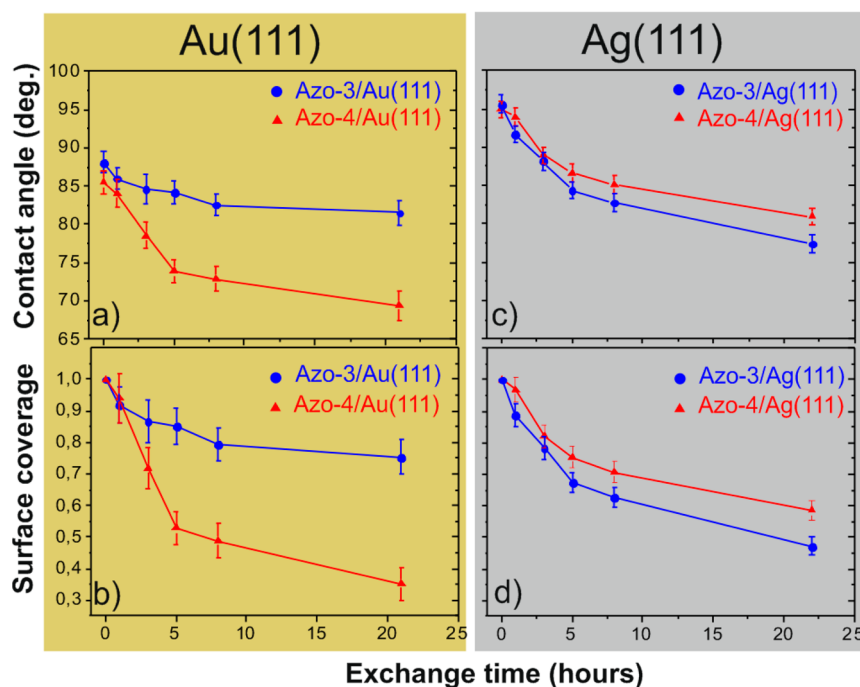


Figure 9. Advancing water contact angle (a, c) and the corresponding surface coverage (b, d) of the Azo-*n* molecules derived in the course of the exchange reaction between the molecules in the Azo-*n* SAMs on Au(111) (left) or Ag(111) (right) and the MHDA molecules in solution. See text for details.

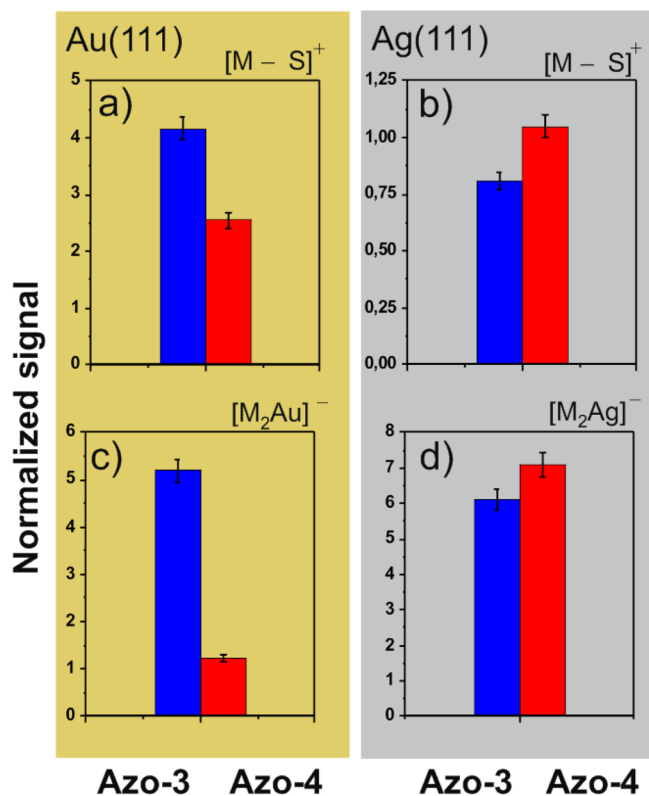


Figure 10. Results of the S-SIMS data analysis for the Azo-3 (blue bars) and Azo-4 (red bars) SAMs prepared on Au(111) (left) and Ag(111) (right). (a and b) Normalized signal of the [M - S]⁺ secondary ion related to the emission of desulfurized molecular fragment (i.e., molecular backbone). (c and d) Normalized signals of the [M₂Au]⁻ and [M₂Ag]⁻ secondary ions related to the emission of the molecule–metal clusters.

17%) signal was measured for the Azo-4 SAM as compared to the Azo-3 monolayer.

4. DISCUSSION

Both microscopic and spectroscopic data exhibit pronounced and well-reproducible odd–even effects in the packing density and molecular inclinations of the Azo-*n* SAMs on Au(111) and Ag(111).

We start a detailed discussion with a structural analysis of the Azo-3 and Azo-4 films on Au(111). The STM data obtained for Azo-3/Au(111) indicate formation of a very well ordered ($2\sqrt{3} \times 1.14\sqrt{3}$)R30° lattice which is close to the commensurate ($2\sqrt{3} \times \sqrt{3}$)R30° structure reported previously for the odd-numbered biphenyl^{12,13} and terphenyl¹⁷-substituted AT SAMs. The ($2\sqrt{3} \times 1.14\sqrt{3}$)R30° arrangement in Azo-3/Au(111) can be compared to the monoclinic lattice of azobenzene in the bulk state.¹⁰⁴ Within this layered structure, azobenzene molecules form a herringbone packing in the (001) plane.¹⁰⁴ The oblique, two-dimensional unit cell of such a herringbone arrangement can be described by the vectors **a** = 0.578 nm and **b** = 1.348 nm defined as in the corresponding ($2\sqrt{3} \times 1.14\sqrt{3}$)R30° lattice of Azo-3/Au(111) (**a** = 0.568 nm and **b** = 0.997 nm). A comparison of these two structures clearly shows that along the **a** vector both structures are essentially identical within the precision of our STM data. In contrast, along the **b** vector, the Azo-3/Au(111) lattice is significantly shorter as compared to the bulk arrangement. As a result, the molecular footprint associated with the azobenzene moieties within the (001) plane of the bulk crystal amounts to ca. 0.353 nm², which is ca. 43% larger as compared to the analogous value for the ($2\sqrt{3} \times 1.14\sqrt{3}$)R30° lattice of Azo-3/Au(111). On first sight this is quite a surprising result, as one would expect much lower if any differences. However, the molecular footprint is not the only parameter which one needs to consider on comparing the structure of Azo-3/Au(111) with the (001) crystal plane of

bulk azobenzene. Another important factor is the tilt angle of the molecular backbone. In this context, we note that the large molecular footprint of azobenzene molecules in the (001) crystal plane of bulk azobenzene is associated with a quite large tilt angle of 54° measured with respect to the normal to the (001) plane.¹⁰⁴ Accordingly, the much smaller footprint in Azo-3/Au(111) can be associated with the much smaller molecular tilt which, according to the NEXAFS data, amounts to only $\sim 20^\circ$. Considering the molecular footprint, tilt angle, and length of the azobenzene unit (1.097 nm)¹⁰⁴ together, one can calculate the volume per azobenzene molecule in the (001) layer of bulk azobenzene (0.227 nm^3) and compare it with the corresponding volume ($\sim 0.253\text{ nm}^3$) per azobenzene moiety in Azo-3/Au(111). Both values are quite similar, even though the latter one is slightly (by ca. 10%) higher. We therefore conclude that both the packing motive (herringbone pattern) as well as the volume density of the azobenzene moieties in the Azo-3 SAMs on Au(111) mimic those in the (001) plane of the azobenzene crystal with, however, modification of the 2D unit cell dimensions along the **b** vector and the associated change in the molecular tilt to adjust to the Au(111) substrate lattice along this direction. In contrast, along the short **a** vector, which defines the spacing to the next neighbors, the azobenzene moieties in the SAM preserve the distance characteristic of the bulk crystal and, thus, form, in this direction, an incommensurate structure with the Au(111) substrate. Such unidirectional mismatch leads to the appearance of surface stress that has to be relaxed by, e.g., formation of line defects crossing the ordered domains at characteristic angle to the direction of the **a** vector. Indeed, supporting such a prediction and our general considerations, the STM images reveal additional features in the form of bright bands which cross the ($2\sqrt{3} \times 1.14\sqrt{3}$)R30° structure at a fixed angle of 60° with respect to the **a** vector, i.e., along another equivalent $11\bar{2}$ high-symmetry direction of the Au(111) substrate. Importantly, formation of such bright bands does not disturb the molecular lattice as follows from the STM data. Note that the same effect has been observed before for odd-numbered biphenyl-terminated alkanethiols¹⁰ and alkaneselenols²¹ on Au(111) substrate. We attribute this additional pattern to the domain boundaries (solitons in Frenkel–Kontorova model¹⁰⁵) at the molecule–substrate interface as a form of stress relaxation in hybrid araliphatic SAMs.¹⁰ As proposed in the previous study,¹⁰ the presence of the aliphatic linker between the aromatic moiety and the substrate gives the possibility to leave the aromatic structure to a large extent unaffected and relax this stress by a combination of factors involving conformational degrees of freedom of the spacer and deviations of the headgroup (thiolate) lattice from a perfect commensurate structure, which leads to formation of additional domain boundaries (solitons) at the SAM–substrate interface.

The STM data obtained for the Azo-4/Au(111) sample show formation of the incommensurate ($2\sqrt{3} \times 1.30\sqrt{3}$)R30° lattice (Figure 3). The change in the parity of the number of the CH_2 units in the aliphatic linker from odd to even resulted in a significant structural distortion of the molecular structure as compared to Azo-3/Au(111). The intermolecular spacing along the **a** vector increased from 0.57 to 0.65 nm, which makes this structure even more expanded than in the Azo-3 case. Importantly, in contrast to the Azo-3/Au(111) lattice, this spacing is also inconsistent with the respective distance (0.578 nm) in the (001) plane of bulk azobenzene. Thus, in this case we have a structure which, along the **a** vector, fits neither with

the substrate nor with the molecular crystal lattice. As a result, significant unidirectional stress can appear, with relaxation via formation of line defects which should cross the ordered molecular domains at a characteristic angle to the direction of the **a** vector. This assumption is again fully consistent with the STM data (Figure 3d and 3f), which indeed show formation of a dense network of line defects crossing the ($2\sqrt{3} \times 1.30\sqrt{3}$)R30° structure at a fixed angle of 60° with respect to the **a** vector, i.e., along another equivalent $11\bar{2}$ high-symmetry direction of the Au(111) substrate. Importantly, the orientation of these line defects with respect to the molecular lattice is exactly the same as in the case of Azo-3/Au(111), but their nature is fundamentally different. Whereas in the latter case these defects are in the form of domain boundaries (solitons) at the SAM–substrate interface, with no distortion of the molecular structure, this structure is directly affected by the defects for Azo-4/Au(111). One can then assume that the stress relaxation via conformational degrees of freedom of the spacer and/or deviations of the headgroup lattice would be insufficient for the stress release in the Azo-4 monolayers. This makes relaxation via breaking the periodicity of the molecular structure necessary.

The molecular footprint in Azo-4/Au(111) ($\sim 0.281\text{ nm}^2$) is larger than that in Azo-3/Au(111) ($\sim 0.246\text{ nm}^2$). A respective difference of ca. 14% is fully consistent with the HRXPS data which show ca. 14–15% lower effective thickness of the former film compared to the latter, corresponding to a lower packing density and, consequently, larger molecular footprint in Azo-4/Au(111). At the same time, this footprint, similarly to the case of Azo-3/Au(111), is much smaller as compared to the respective value for the (001) plane of bulk azobenzene (0.353 nm^2). As discussed above, considering additionally the tilt angle ($\sim 37^\circ$) of the azobenzene moiety in Azo-4/Au(111) obtained from the NEXAFS data (Table 1), one can compare the volume per azobenzene moiety in this structure ($\sim 0.246\text{ nm}^3$) with the respective values for Azo-3/Au(111) ($\sim 0.253\text{ nm}^3$) and the (001) plane of the bulk azobenzene (0.227 nm^3). This comparison shows that the values obtained for both types of monolayers are very similar and, as mentioned above, somewhat lower (ca. 10%) than in the crystal structure.

In the second set of experiments, the relative stability of the Azo-3 and Azo-4 SAMs was studied using two independent methods, i.e., dedicated exchange experiments and ion-induced desorption. In the case of the Au(111) substrate, the exchange experiments exhibited much higher stability of the Azo-3 SAM toward the exchange by the MHDA molecules than for the Azo-4 monolayer. This odd–even effect in stability is fully consistent with the results of the microscopic and spectroscopic structural analysis showing higher packing density and lower concentration of defects in the Azo-3 film as compared to the Azo-4 monolayer. Since the exchange process involves cleavage of the bond between the Azo-*n* molecules and the substrate (Au–S), higher stability of this bond for Azo-3/Au(111) as compared to Azo-4/Au(111) can be assumed. This conclusion is additionally supported by the S-SIMS data. The $[\text{M} - \text{S}]^+$ secondary ion, associated with the molecular backbone of Azo-*n*, originates from cleavage of the S–C bond representing, thus, a fingerprint of its stability.^{93,97} Significantly, this stability is directly related to the stability of the adjacent S–Au bond because of the redistribution of the electron density between these bonds.^{93,97} Accordingly, lower stability of the S–C bond is accompanied by a higher stability of the S–Au bond and vice versa. Thus, a higher intensity of the $[\text{M} - \text{S}]^+$ signal for Azo-

3/Au(111) as compared to Azo-4/Au(111) indicates lower stability of the C–S bond but higher stability of the S–Au bond in the former case, fully consistent with the conclusion reached on the basis of the exchange experiments. The odd–even difference in stability of Azo-3/Au(111) and Azo-4/Au(111) is also visible in relative intensity of $[M_2Au]^-$ molecule–metal clusters emission. This signal, which is a well-known fingerprint of SAMs formation in S-SIMS technique, shows ca. 4 times higher emission in the case of Azo-3/Au(111). Despite a much more complicated scenario leading to its formation⁹⁹ the existence of this ion relies on stability of the molecule–metal bond; therefore, higher signal intensity for Azo-3/Au(111) can be, tentatively, correlated with the higher stability of the S–Au bonding for this SAM.

The close correlation of the exchange experiments and S-SIMS data was also observed in the experiments performed for the Azo-*n* SAMs on Ag(111). In this case, the exchange data show the reverse (as compared to the Au substrate) but much smaller difference in stability between the Azo-3 and the Azo-4 monolayers, with slightly higher stability for the latter film. This observation is confirmed by the S-SIMS data, which show an inverse, as compared to the case of Au(111), relation in the intensity of both $[M - S]^+$ and $[M_2Ag]^-$ ions, indicating a higher stability of the S–Ag bond for Azo-4/Ag(111) as compared to Azo-3/Ag(111). This reversed but smaller odd–even effect in the film stability for the Ag(111) substrate correlates well with the structural data. In particular, the NEXAFS results suggest not only inversion of the odd–even effect, in terms of molecular inclination, at going from Au(111) to Ag(111) but also its certain reduction, i.e., an average tilt angle difference of 8° for Ag(111) as compared to 17° for Au(111). The reverse odd–even effect in the effective film thickness is also clearly visible in the HRXPS data obtained for the Azo-*n* films on Ag(111). However, in contrast to the tilt angle and stability data, the odd–even difference in this parameter is similar for the case of Au(111) and Ag(111) substrates. We note here that the estimated odd–even difference in the effective film thickness of ca. 0.20 nm for the Au(111) and 0.25 nm for the Ag(111) substrates is in any case small considering the quite limited precision of the respective evaluation procedure, which is ca. ± 0.1 nm.

In the final part of our discussion we would like to address the factors behind the structural odd–even effects observed for the Azo-*n* monolayers on Au(111) and Ag(111) and their apparent impact on the film stability. Following the argumentation of the previous studies on biphenyl- and terphenyl-substituted alkanethiol^{12–18} and alkaneselenol^{21–23} SAMs on the same substrates, the observed odd–even effects in the Azo-*n* films can be related to the existence of so-called bending potential, associated with a preferable geometry of the substrate–S–C joint. This configuration is then transmitted, via the all-trans-configured aliphatic linker, $(CH_2)_m$, to the terminal azobenzene moiety, with the parity of *n* being the decisive parameter, defining the spatial orientation of the last segment of the linker, mimicked by the adjacent azobenzene unit. Thus, the molecular inclination of the azobenzene unit, given by the average tilt angle, depends directly on the parity of *n*, as shown schematically in Figure 11. Consequently, larger or smaller inclination results in a larger or smaller intermolecular spacing (Figure 11), respectively, as reflected in the molecular footprint and the effective packing density.

Importantly, the preferred bonding configurations of the headgroups are distinctly different for the Au(111) and

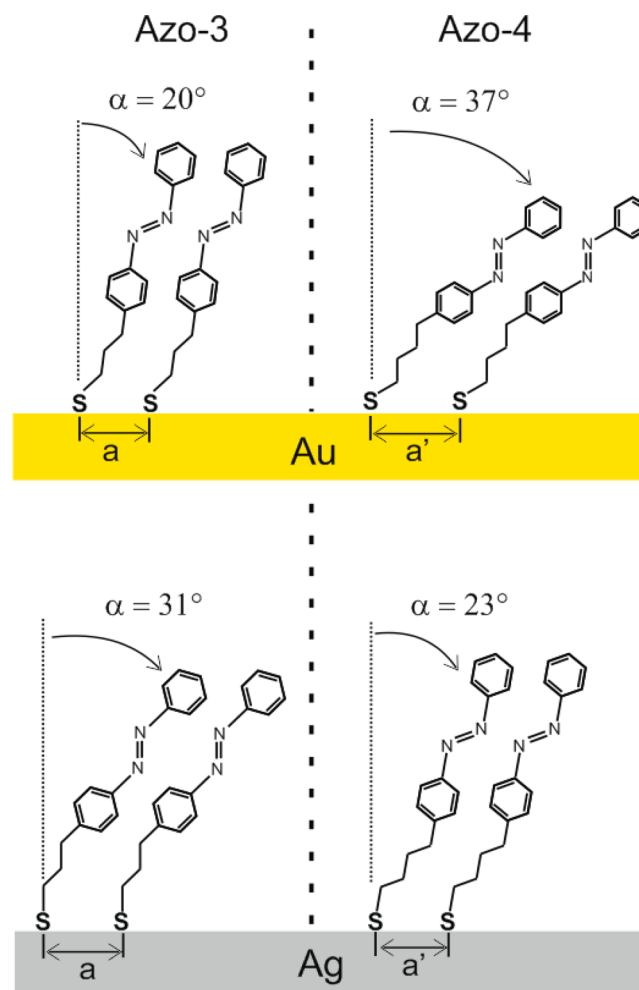


Figure 11. Schematic presentation of the odd–even effect for the Azo-3 and Azo-4 SAMs on Au(111) (top) and Ag(111) (bottom) with indication of the corresponding changes in the molecular tilt and the distances between the molecules (*a* and *a'* are related to the Azo-3 and Azo-4 adsorbates, respectively).

Ag(111) substrates, with the optimal values of the substrate–S–C angle close to 104° and 180°, respectively.^{12–17} Accordingly, the phase of the odd–even effects with respect to the parity of *n* should be reversed for the SAMs on Au(111) and Ag(111) as was indeed reported for the biphenyl- and terphenyl-substituted alkanethiols^{12–18} and alkaneselenols.^{21–23} The same reversal is now observed for the Azo-*n* monolayers, assuming the applicability of the above model also to these systems as well as the generality of the odd–even behavior for substituted alkanethiol and alkaneselenol monolayers on noble metal substrates. To our knowledge the only reported exceptions are anthracene-substituted SAMs, where the odd–even effects are compensated by the rotation of the anthracene backbone, attached nonsymmetrically to the headgroup.¹⁰⁶

A very important aspect of the odd–even effects is that the preferable orientation, associated with the bending potential, is not mimicked completely by the SAM constituents. Instead, the bending potential enters the balance of the structure-building interactions working either cooperatively or competitively with them.³¹ A cooperative balance occurs at the parity of *n* corresponding to the small molecular inclination of the substitutions, correlating with the thermodynamical drive for the dense molecular packing. A competitive situation takes

place if the parity of n corresponds to the large molecular inclination of the substitutions, diminishing the thermodynamically favorable, dense molecular packing. In this case, an intermediate structural configuration will be achieved, with a deviation from the optimal substrate–S–C angle, hindering the extent of the odd–even effects. Significantly, the deviation from the optimal substrate–S–C angle will put some stress on the substrate–S bond, resulting in the change of its energetics,¹⁵ which, along with the lower packing density, leads to lower stability toward electrochemical desorption,^{24,25} ion-induced desorption,²⁶ electron irradiation,²⁷ exchange reaction (analogous to the one presented here),^{28,29} and thermally induced phase transitions.^{30–33} In all these experiments, probing different aspects of film stability for biphenyl-terminated alkanethiols and alkaneselenols on the Au(111) substrate, higher stability of the odd-numbered homologues was correlated with higher packing density (microscopic and spectroscopic data) and higher stability of the Au–S bond (exchange and ion desorption experiments) as compared to even-numbered SAMs. The same effect is observed here for Azo- n /Au(111). Since the molecule–substrate chemical bonding and intermolecular interactions are considered to be two main contributors to the SAMs energetics, the increase in the strength and the number of Au–S bonds per unit area is thus fully consistent with the enhanced stability of the odd-numbered homologue. In the present study, however, an additional factor affecting the film stability becomes perceptible, contributing to the higher stability of the odd-numbered homologue on the Au(111) substrate. It is the surface stress, which is sufficiently low for Azo-3/Au(111) due to a partial relaxation by formation of the solitons at the SAM–substrate interface (see above), but apparently high for Azo-4/Au(111) characterized by the distinctly noncommensurate structure, with high density of line defects.

The odd–even effect in stability for the case of the Ag(111) substrate has not been reported in the literature so far. However, considering the close correlation between the structural odd–even effect on the Au(111) substrate and the respective odd–even effect in the film stability, an analogous behavior could be expected for Ag(111) as well with, however, reversed phase with respect to the parity of n . Indeed, the presented exchange and ion desorption data obtained for the Ag(111) substrate show reversed, as compared to the Au(111) case, relation in stability between the odd- and the even-numbered homologues. However, the odd–even effects in stability observed for the Ag(111) substrate are smaller as compared to the Au(111) case. Such a behavior can be probably related to two factors: (i) a stronger S–Ag bond as compared to the S–Au bond in aliphatic SAMs (concluded from electrochemical desorption,¹⁰⁷ thermal desorption,¹⁰⁸ and DFT calculations^{1,109}) and (ii) smaller corrugation of the S–substrate binding energy hypersurface^{1,109} for Ag(111) as compared to Au(111). The stronger S–substrate bond is more difficult to disrupt, resulting in a smaller impact of the structural odd–even effects on its stability. The smaller corrugation of the S–substrate binding energy hypersurface can be associated with a lower impact of a noncommensurate molecular arrangement and lower surface stress, once again reducing the difference in stability between the odd- and the even-numbered films on the Ag(111) surface as compared to Au(111).

5. CONCLUSIONS

In summary, we performed a detailed structural analysis of prototypical SAMs containing an azobenzene moiety linked to the thiol headgroup via a short aliphatic spacer of variable length, i.e., $(\text{CH}_2)_3$ or $(\text{CH}_2)_4$, corresponding to the different parity of n . These SAMs were prepared on the Au(111) and Ag(111) substrates. For both these substrates, a pronounced and well-reproduced dependence of the packing density and molecular inclination on the parity of n was observed. For Au(111), higher packing density and smaller inclination of the azobenzene moieties occurred for the films with n = odd as compared to the case of the even n . For Ag(111), this relation was reversed, i.e., higher packing density and lower molecular inclination was found for the even-numbered system as compared to the odd-numbered one. This behavior goes in line with well-known odd–even effects in molecular assemblies, reported previously for a variety of oligophenyl-substituted AT SAMs and observed now for the azobenzene-substituted monolayers as well. Such a finding underlines the generality of these effects, related to the existence of the substrate-specific bending potential at the substrate–headgroup–C joint and representing an important factor for the design of functional monolayers on metal and semiconductor substrates.

Detailed information about the molecular arrangements in the azobenzene-substituted SAMs, including the parameters of the unit cells and the character and density of defects, could be obtained for the case of Au(111). On Ag(111), analogous structures can be assumed, based on the similarity of the spectroscopic results for the SAMs on both substrates (considering lack of high-resolution STM data in this case, part of this missing information could be provided by a future diffraction study, e.g., LEED or grazing incidence XRD). Considering quite dense molecular packing in all films studied, a dominant trans conformation of the azobenzene moieties can be expected.

In addition to the structural characterization, the stability of the azobenzene-substituted SAMs was studied by exchange and ion desorption experiments, probing specifically the substrate–S bond. This stability exhibited the odd–even behavior as well, i.e., higher stability of the odd-numbered film on Au(111) and the even-numbered film on Ag(111) as compared to their counterparts with the different parity. Observed behavior correlates perfectly with the structural odd–even effects, with lower stability being a consequence of the stressed S–substrate bond, lower surface coverage, and higher surface stress. The odd–even effect in film stability is smaller for the Ag(111) substrate as compared to Au(111), which could be explained by the higher S–substrate binding energy and lower corrugation of the S–Ag(111) binding energy hypersurface as compared to the S–Au(111).

The possibility to adjust the packing density of azobenzene-substituted SAMs by using the odd–even effects can be of importance for their isomerization behavior upon exposure to UV and visible light, even though it is not clear whether the respective packing density differences are large enough to influence this behavior. The highly ordered molecular arrangements in the Azo-3 and Azo-4 SAMs can be of both advantage and disadvantage for the extent of isomerization, depending on the realization of either individual or correlated (collective) response to the external stimuli. This should be the subject of further investigations, along with the effect of additional tailgroups attached to the azobenzene moiety.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b07899.

S-SIMS mass spectra for the Azo-3(4) SAMs on Au(111) and Ag(111) substrates (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*Phone: +49 6221 54 4921. Fax: +49 6221 54 6199. E-mail: Michael.Zharnikov@urz.uni-heidelberg.de.

*Phone: +48 12 6644520. Fax: +48 12 664 4905. E-mail: piotr.cyganik@uj.edu.pl.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

P.C. and D.A. thank Prof. Marek Szymonski for providing access to the STM in the Department of Physics of Nanostructures and Nanotechnology at the Jagiellonian University. S.S. and M.Z. thank the Bessy II and Max-IV staff and A. Preobrajenski, in particular, for the technical support during the synchrotron-based experiments as well as A. Nefedov and Ch. Wöll for the technical cooperation at Bessy II. This work was supported financially by the National Science Centre Poland (grant DEC-2013/10/E/ST5/00060), the Innovation Fond "Frontier" of the Heidelberg University, and the Deutsche Forschungsgemeinschaft (grant ZH 63/17-1) and by funding from the European Community's Seventh Framework Programme (FP7/2007-2013) CALIPSO under grant agreement no. 312284. The S-SIMS equipment was purchased with the financial support of the European Regional Development Fund (grant POIG.02.02.00-12-023/08).

■ REFERENCES

- (1) Ulman, A. Formation and Structure of Self-Assembled Monolayers. *Chem. Rev.* **1996**, *96*, 1533–1554.
- (2) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chem. Rev.* **2005**, *105*, 1103–1170.
- (3) Orgiu, E.; Samori, P. Organic Electronics Marries Photochromism: Generation of Multifunctional Interfaces, Materials, and Devices. *Adv. Mater.* **2014**, *26*, 1827–1845.
- (4) Coskun, A.; Spruell, J. M.; Barin, G.; Dichtel, W. R.; Flood, A. H.; Bartos, Y. Y.; Stoddart, J. F. High Hopes Can Molecular Electronics Realise its Potential? *Chem. Soc. Rev.* **2012**, *41*, 4827–4859.
- (5) Song, H.; Reed, M. A.; Lee, T. Single Molecule Electronic Devices. *Adv. Mater.* **2011**, *23*, 1583–1608.
- (6) Meyerbröker, N.; Li, Z.-A.; Eck, W.; Zharnikov, M. Biocompatible Nanomembranes Based on PEGylation of Cross-Linked Self-Assembled Monolayers. *Chem. Mater.* **2012**, *24*, 2965–2972.
- (7) Angelova, P.; Vieker, H.; Weber, N. E.; Matei, D.; Reimer, O.; Meier, I.; Kurasch, S.; Biskupek, J.; Lorbach, D.; Wunderlich, et al. Universal Scheme to Convert Aromatic Molecular Monolayers into Functional Carbon Nanomembranes. *ACS Nano* **2013**, *7*, 6489–6497.
- (8) Azzam, W.; Fuxen, C.; Birkner, A.; Rong, H. T.; Buck, M.; Wöll, C. Coexistence of Different Structural Phases in Thioaromatic Monolayers on Au(111). *Langmuir* **2003**, *19*, 4958–4968.
- (9) Käfer, D.; Witte, G.; Cyganik, P.; Terfort, A.; Wöll, C. A Comprehensive Study of Self-Assembled Monolayers of Anthracene Thiol on Gold: Solvents Effects, Structure and Stability. *J. Am. Chem. Soc.* **2006**, *128*, 1723–1732.
- (10) Cyganik, P.; Buck, M.; Wilton-Ely, J. D.; Wöll, C. Stress in Self-Assembled Monolayers: ω -biphenyl Alkane Thiols on Au(111). *J. Phys. Chem. B* **2005**, *109*, 10902–10908.
- (11) Zharnikov, M.; Frey, S.; Rong, H.-T.; Yang, Y.-J.; Heister, K.; Buck, M.; Grunze, M. The Effect of the Sulfur-Metal Bond on the Structure of Self-Assembled Monolayers. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3359–3362.
- (12) Azzam, W.; Cyganik, P.; Witte, G.; Buck, M.; Wöll, C. Pronounced Odd-Even Changes in the Molecular Arrangement and Packing Density of Biphenyl-Substituted Alkanethiol SAMs. *Langmuir* **2003**, *19*, 8262–8270.
- (13) Cyganik, P.; Buck, M.; Azzam, W.; Wöll, C. Self-Assembled Monolayers of ω -Biphenyl-Alkane Thiols on Au(111): Influence of Spacer Chain on Molecular Packing. *J. Phys. Chem. B* **2004**, *108*, 4989–4969.
- (14) Heister, K.; Zharnikov, M.; Grunze, M.; Johansson, L. S. O. Adsorption of Alkanethiols and Biphenylthiols on Au and Ag Substrates: A High-Resolution X-ray Photoelectron Spectroscopy Study. *J. Phys. Chem. B* **2001**, *105*, 4058–4061.
- (15) Heister, K.; Rong, H. T.; Buck, M.; Zharnikov, M.; Grunze, M.; Johansson, L. S. O. Odd-Even Effects at the S-Metal Interface and in the Aromatic Matrix of Biphenyl-Substituted Alkanethiol Self-Assembled Monolayers. *J. Phys. Chem. B* **2001**, *105*, 6888–6894.
- (16) Rong, H. T.; Frey, S.; Yang, Y. J.; Zharnikov, M.; Buck, M.; Wühn, M.; Wöll, C.; Helmchen, G. On the Importance of the Headgroup Substrate Bond in Thiol Monolayers: A Study of Biphenyl-Based Thiols on Gold and Silver. *Langmuir* **2001**, *17*, 1582–1593.
- (17) Azzam, W.; Bashir, A.; Terfort, A.; Strunskus, T.; Wöll, C. Combined STM and FTIR Characterization of Terphenylalkane Thiol Monolayers on Au(111): Effect of Alkyl Chain Length and Deposition Temperature. *Langmuir* **2006**, *22*, 3647–3655.
- (18) Shaporenko, A.; Brunnbauer, M.; Terfort, A.; Grunze, M.; Zharnikov, M. Structural Forces in Self-Assembled Monolayers: Terphenyl-Substituted Alkanethiols on Noble Metal Substrates. *J. Phys. Chem. B* **2004**, *108*, 14462–14469.
- (19) Chesneau, F.; Schüpbach, B.; Szelagowska-Kunstman, K.; Ballav, N.; Cyganik, P.; Terfort, A.; Zharnikov, M. Self-Assembled Monolayers of Perfluoroterphenyl-Substituted Alkanethiols: Specific Characteristics and Odd–Even Effects. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12123–12137.
- (20) Schüpbach, B.; Bolte, M.; Zharnikov, M.; Terfort, A. Grafting Organic n-Semiconductors to Surfaces: (Perfluoro-p-terphenyl-4-yl)alkane thiols. *Eur. J. Org. Chem.* **2010**, *2010*, 3041–3048.
- (21) Cyganik, P.; Szelagowska-Kunstman, K.; Terfort, A.; Zharnikov, M. Odd-Even Effect in Molecular Packing of Biphenyl-Substituted Alkaneselenol Self-Assembled Monolayers on Au(111): Scanning Tunneling Microscopy Study. *J. Phys. Chem. C* **2008**, *112*, 15466–15473.
- (22) Weidner, T.; Shaporenko, A.; Müller, J.; Schmid, T.; Cyganik, P.; Terfort, A.; Zharnikov, M. The Effect of the Bending Potential on Molecular Arrangement in Alkaneselenolate Self-Assembled Monolayers. *J. Phys. Chem. C* **2008**, *112*, 12495–12506.
- (23) Shaporenko, A.; Müller, J.; Weidner, T.; Terfort, A.; Zharnikov, M. Balance of Structure-Building Forces in Selenium-Based Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2007**, *129*, 2232–2233.
- (24) Long, Y. T.; Rong, H. T.; Buck, M.; Grunze, M. Odd-Even Effects in the Cyclic Voltammetry of Self-Assembled Monolayers of Biphenyl Based Thiols. *J. Electroanal. Chem.* **2002**, *524*, 62–67.
- (25) Thom, I.; Buck, M. Electrochemical Stability of Self-Assembled Monolayers of Biphenyl Based Thiols Studied by Cyclic Voltammetry and Second Harmonic Generation. *Surf. Sci.* **2005**, *581*, 33–46.
- (26) Vervaecke, F.; Wycawska, S.; Cyganik, P.; Bastiaansen, J.; Postawa, Z.; Silverans, R. E.; Vandeweert, E.; Lievens, P. Odd-Even Effects in Ion-Beam-Induced Desorption of Biphenyl-Substituted Alkanethiol Self-Assembled Monolayers. *ChemPhysChem* **2011**, *12*, 140–144.
- (27) Frey, S.; Rong, H. T.; Heister, K.; Yang, Y. J.; Buck, M.; Zharnikov, M. Response of Biphenyl-Substituted Alkanethiol Self-

Assembled Monolayers to Electron Irradiation: Damage Suppression and Odd-Even Effects. *Langmuir* **2002**, *18*, 3142–3150.

(28) Felgenhauer, T.; Rong, H. T.; Buck, M. Electrochemical and Exchange Studies of Self-Assembled Monolayers of Biphenyl Based Thiols on Gold. *J. Electroanal. Chem.* **2003**, *550*, 309–319.

(29) Szelagowska-Kunzman, K.; Cyganik, P.; Schüpbach, B.; Terfort, A. Relative Stability of Thiol and Selenol Based SAMs on Au(111) - Exchange Experiments. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4400–4406.

(30) Cyganik, P.; Buck, M. Polymorphism in Biphenyl-Based Self-Assembled Monolayers of Thiols. *J. Am. Chem. Soc.* **2004**, *126*, 5960–5961.

(31) Cyganik, P.; Buck, M.; Strunskus, T.; Shaporenko, A.; Wilton-Ely, J. D. E. T.; Zharnikov, M.; Wöll, C. Competition as a Design Concept: Polymorphism in Self-Assembled Monolayers of Biphenyl-Based Thiols. *J. Am. Chem. Soc.* **2006**, *128*, 13868–13878.

(32) Cyganik, P.; Buck, M.; Strunskus, T.; Shaporenko, A.; Witte, G.; Zharnikov, M.; Wöll, C. Influence of Molecular Structure on Phase Transitions: A Study of Self-Assembled Monolayers of 2-(Aryl)-Ethane Thiols. *J. Phys. Chem. C* **2007**, *111*, 16909–16919.

(33) Dendzik, M.; Terfort, A.; Cyganik, P. Odd-even Effect in the Polymorphism of Self-Assembled Monolayers of Biphenyl-Substituted Alkaneselenolates on Au(111). *J. Phys. Chem. C* **2012**, *116*, 19535–19542.

(34) Tao, F.; Bernasek, S. L. Understanding Odd-Even Effects in Organic Self-Assembled Monolayers. *Chem. Rev.* **2007**, *107*, 1408–1453.

(35) Thuo, M. M.; Reus, W. F.; Nijhuis, C. A.; Barber, J. R.; Kim, C.; Schulz, M. D.; Whitesides, G. M. Odd-Even Effects in Charge Transport across Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2011**, *133*, 2962–2975.

(36) Beghbanzadeh, M.; Simeone, F. C.; Bowers, C. M.; Liao, K. C.; Thuo, M.; Baghbanzadeh, M.; Miller, M. S.; Carmichael, T. B.; Whitesides, G. M. Odd-Even Effects in Charge Transport across n-Alkanethiolate-Based SAMs. *J. Am. Chem. Soc.* **2014**, *136*, 16919–16925.

(37) Fracasso, D.; Muglali, M. I.; Rohwerder, M.; Terfort, A.; Chiechi, R. C. Influence of an Atom in EGaIn/Ga₂O₃ Tunneling Junctions Comprising Self-Assembled Monolayers. *J. Phys. Chem. C* **2013**, *117*, 11367–11376.

(38) Yuan, L.; Thompson, D.; Cao, L.; Nerngchangnong, N.; Nijhuis, C. A. One Carbon Matters: The Origin and Reversal of Odd-Even Effects in Molecular Diodes with Self-Assembled Monolayers of Ferrocenyl-Alkanethiolates. *J. Phys. Chem. C* **2015**, *119*, 17910–17919.

(39) Jiang, L.; Sangeeth, C. S. S.; Nijhuis, C. A. The Origin of the Odd-Even Effect in the Tunneling Rates across EGaIn Junctions with Self-Assembled Monolayers (SAMs) of n-Alkanethiolates. *J. Am. Chem. Soc.* **2015**, *137*, 10659–10667.

(40) Shaporenko, A.; Elbing, M.; Blaszczyk, A.; von Hänisch, C.; Mayor, M.; Zharnikov, M. Self-Assembled Monolayers from Biphenyldithiol Derivatives: Optimization of the Deprotection Procedure and Effect of the Molecular Conformation. *J. Phys. Chem. B* **2006**, *110*, 4307–4317.

(41) Russew, M.; Hecht, S. Photoswitches: From Molecules to Materials. *Adv. Mater.* **2010**, *22*, 3348–3360.

(42) Ferri, V.; Pace, G.; Dickey, M. D.; Zharnikov, M.; Samori, P.; Mayor, M.; Rampi, M. A. Light-Powered Electrical Switch Based on Cargo-Lifting Azobenzene Monolayers. *Angew. Chem., Int. Ed.* **2008**, *47*, 3407–3409.

(43) Weber, T.; Chandrasekaran, V.; Stamer, I.; Thygesen, M. B.; Terfort, A.; Lindhorst, T. K. Switching of Bacterial Adhesion to a Glycosylated Surface by Reversible Reorientation of the Carbohydrate Ligand. *Angew. Chem., Int. Ed.* **2014**, *53*, 14583–14586.

(44) Pace, G.; Ferri, V.; Grave, C.; Elbing, M.; Zharnikov, M.; Mayor, M.; Rampi, M. A.; Samori, P. Cooperative Light-Induced Molecular Movements of Highly Ordered Azobenzene Self-Assembled Monolayers. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 9937–9942.

(45) Crivillers, N.; Liscio, A.; Di Stasio, F.; Van Dyck, C.; Osella, S.; Cornil, D.; Mian, S.; Lazzarini, G. M.; Fenwick, O.; Orgiu, et al. Photoinduced Work Function Changes by Isomerization of a Densely

Packed Azobenzene-Based SAM on Au: a Joint Experimental and Theoretical Study. *Phys. Chem. Chem. Phys.* **2011**, *13*, 14302–14310.

(46) Mativetsky, J. M.; Pace, G.; Elbing, M.; Rampi, M. A.; Mayor, M.; Samori, P. Azobenzenes as Light-Controlled Molecular Electronic Switches in Nanoscale Metal-Molecule-Metal Junctions. *J. Am. Chem. Soc.* **2008**, *130*, 9192–9193.

(47) Crivillers, N.; Orgiu, E.; Reinders, F.; Mayor, M.; Samori, P. Optical Modulation of the Charge Injection in an Organic Field-Effect Transistor Based on Photochromic Self-Assembled-Monolayer-Functionalized Electrodes. *Adv. Mater.* **2011**, *23*, 1447.

(48) Faramarzi, V.; Raimondo, C.; Reinders, F.; Mayor, M.; Samori, P.; Doudin, B. Optically Switchable Molecular Device Using Microsphere Based Junctions. *Appl. Phys. Lett.* **2011**, *99*, 233104.

(49) Elbing, M.; Blaszczyk, A.; Hänisch, C.; Mayor, M.; Ferri, V.; Grave, C.; Rampi, M. A.; Pace, G.; Samori, P.; Shaporenko, A.; et al. Single Component Self-Assembled Monolayers of Aromatic Azobiphenyl: Influence of the Packing Tightness on the SAM Structure and Light-Induced Molecular Movements. *Adv. Funct. Mater.* **2008**, *18*, 2972–2983.

(50) Heinemann, N.; Grunau, J.; Leisner, T.; Andreyev, O.; Kuhn, S.; Jung, U.; Zargarani, D.; Herges, R.; Magnussen, O.; Bauer, M. Reversible Switching in Self-Assembled Monolayers of Azobenzene Thiolates on Au (111) Probed by Threshold Photoemission. *Chem. Phys.* **2012**, *402*, 22–28.

(51) Jung, U.; Filinova, O.; Kuhn, S.; Zargarani, D.; Bornholdt, C.; Herges, R.; Magnussen, O. Photoswitching Behavior of Azobenzene-Containing Alkanethiol Self-Assembled Monolayers on Au Surfaces. *Langmuir* **2010**, *26*, 13913–13923.

(52) Kim, Y.; Wang, G.; Choe, M.; Kim, J.; Lee, S.; Park, S.; Kim, D. Y.; Lee, B. H.; Lee, T. Electronic Properties Associated with Conformational Changes in Azobenzene-Derivative Molecular Junctions. *Org. Electron.* **2011**, *12*, 2144–2150.

(53) Weidner, T.; Brethauer, F.; Ballav, N.; Motschmann, H.; Orendi, H.; Bruhn, C.; Siemeling, U.; Zharnikov, M. Correlation Between the Molecular Structure and Photoresponse in Aliphatic Self-Assembled Monolayers with Azobenzene Tailgroups. *Langmuir* **2008**, *24*, 11691–11700.

(54) Valley, D. T.; Onstott, M.; Malyk, S.; Benderskii, A. V. Steric Hindrance of Photoswitching in Self-Assembled Monolayers of Azobenzene and Alkane Thiols. *Langmuir* **2013**, *29*, 11623–11631.

(55) Moldt, T.; Brete, D.; Przyrembel, D.; Das, S.; Goldman, J. R.; Kundu, P. K.; Gahl, C.; Klajn, R.; Weinelt, M. Tailoring the Properties of Surface-Immobilized Azobenzenes by Monolayer Dilution and Surface Curvature. *Langmuir* **2015**, *31*, 1048–1057.

(56) Joshi, G. K.; Blodgett, K. N.; Muhoberac, B. B.; Johnson, M. A.; Smith, K. A.; Sardar, R. Ultrasensitive Photoreversible Molecular Sensors of Azobenzene Functionalized Plasmonic Nanoantennas. *Nano Lett.* **2014**, *14*, 532–540.

(57) Zheng, Y. B.; Payton, J. L.; Chung, C. H.; Liu, R.; Cheunkar, S.; Pathem, B. K.; Yang, Y.; Jensen, L.; Weiss, P. S. Surface-Enhanced Raman Spectroscopy to Probe Reversibly Photoswitchable Azobenzene in Controlled Nanoscale Environments. *Nano Lett.* **2011**, *11*, 3447–3452.

(58) Benassi, E.; Corni, S. Quenching of the Photoisomerization of Azobenzene Self-Assembled Monolayers by the Metal Substrate. *J. Phys. Chem. C* **2014**, *118*, 25906–25917.

(59) Gahl, C.; Schmidt, R.; Brete, D.; McNellis, E. R.; Freyer, W.; Carley, R.; Reuter, K.; Weinelt, M. Structure and Excitonic Coupling in Self-Assembled Monolayers of Azobenzene-Functionalized Alkanethiols. *J. Am. Chem. Soc.* **2010**, *132*, 1831–1838.

(60) Jung, U.; Baisch, B.; Kaminski, D.; Krug, K.; Elsen, A.; Weisenstein, T.; Raffa, D.; Stetter, J.; Bornholdt, C.; Herges, R.; et al. Structure and Redox Behavior of Azobenzene-Containing Monolayers on Au(111): A Combined STM, X-ray Reflectivity, and Voltammetry Study. *J. Electroanal. Chem.* **2008**, *619–620*, 152–158.

(61) Krakert, S.; Terfort, A. Preparation of Azobenzenealkaneithiols for Self-Assembled Monolayers with Photoswitchable Properties. *Aust. J. Chem.* **2010**, *63*, 303–314.

- (62) Cyganik, P. Ph.D. Dissertation, Jagiellonian University, Kraków, 2002.
- (63) Satterley, C. J.; Lovelock, K. R. J.; Thom, I.; Dhanak, V. R.; Buck, M.; Jones, R. G. Normal Incidence X-ray Standing Wave Analysis of Thin Gold Films. *Surf. Sci.* **2006**, *600*, 4825.
- (64) Shaporenko, A.; Cyganik, P.; Buck, M.; Ullman, A.; Zharnikov, M. Self-Assembled Monolayers of Semifluorinated Alkaneselenolates on Noble Metal Substrates. *Langmuir* **2005**, *21*, 8204–8213.
- (65) Shaporenko, A.; Cyganik, P.; Buck, M.; Terfort, A.; Zharnikov, M. Self-Assembled Monolayers of Aromatic Selenolates on Noble Metal Substrates. *J. Phys. Chem. B* **2005**, *109*, 13630–13638.
- (66) Zharnikov, M. High-Resolution X-Ray Photoelectron Spectroscopy in Studies of Self-Assembled Organic Monolayer. *J. Electron Spectrosc. Relat. Phenom.* **2010**, *178–179*, 380–393.
- (67) Moulder, J. F.; Stickle, W. E.; Sobol, P. E.; Bomben, K. D. In *Handbook of X-ray Photoelectron Spectroscopy*; Chastian, J., Ed.; Eden Prairie, Perkin-Elmer Corp.: MN, 1992.
- (68) Thome, J.; Himmelhaus, M.; Zharnikov, M.; Grunze, M. *Langmuir* **1998**, *14*, 7435–7446.
- (69) Vickerman, J. C.; Gilmore, I. S. *Surface Analysis-The principal techniques*; Wiley: Chichester, 1997.
- (70) Lamont, C. L. A.; Wilkes, J. Attenuation Length of Electrons in Self-Assembled Monolayers of n-Alkanethiols on Gold. *Langmuir* **1999**, *15*, 2037–2042.
- (71) Stöhr, J. *NEXAFS spectroscopy*; Springer-Verlag: Berlin Heidelberg, 1992.
- (72) Batson, P. E. Carbon-1s Near-Edge-Absorption Fine-Structure in Graphite. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, *48*, 2608–2610.
- (73) Domke, M.; Mandel, T.; Puschmann, A.; Xue, C.; Shirley, D. A.; Kaindl, G.; Petersen, H.; Kuske, P. Performance of the High-Resolution SX700/II Monochromator. *Rev. Sci. Instrum.* **1992**, *63*, 80–89.
- (74) Nefedov, A.; Wöll, C. Advanced Applications of NEXAFS Spectroscopy for Functionalized Surfaces, in *Surface Science Techniques*. In *Springer Series in Surface Science*; Bracco, G., Holst, B., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, 2013; Vol. 51, pp 277–306.
- (75) Cyganik, P.; Vandeweerdt, E.; Postawa, Z.; Bastiaansen, J.; Vervaecke, F.; Lievens, P.; Silverans, R. E.; Winograd, N. Modification and Stability of Aromatic Self-Assembled Monolayers upon Irradiation with Energetic Particles. *J. Phys. Chem. B* **2005**, *109*, 5085–5094.
- (76) Mazzarello, R.; Cossaro, A.; Verdini, A.; Rousseau, R.; Casalis, L.; Danisman, M. F.; Floreano, L.; Scandolo, S.; Morgante, A.; Scoles, G. Structure of a CH₃S Monolayer on Au(111) Solved by the Interplay Between Molecular Dynamics Calculations and Diffraction Measurements. *Phys. Rev. Lett.* **2007**, *98*, 0161021.
- (77) Cossaro, A.; Mazzarello, R.; Rousseau, R.; Casalis, L.; Verdini, A.; Kohlmeier, A.; Floreano, L.; Scandolo, S.; Margante, A.; Klein, M. L.; et al. X-ray Diffraction and Computation Yield the Structure of Alkanethiols on Gold(111). *Science* **2008**, *321*, 943–946.
- (78) Maksymovych, P.; Voznyy, O.; Dougherty, D. B.; Sorescu, D. C.; Yates, J. T. Gold Adatom as a Key Structural Component in Self-assembled Monolayers of Organosulfur Molecules on Au(111). *Prog. Surf. Sci.* **2010**, *85*, 206–240.
- (79) Häkkinen, H. The Gold–sulfur Interface at the Nanoscale. *Nat. Chem.* **2012**, *4*, 443–455.
- (80) Maksymovych, P.; Sorescu, D. C.; Yates, J. T. Gold-Adatom-Mediated Bonding in Self-Assembled Short-Chain Alkanethiolate Species on the Au(111) Surface. *Phys. Rev. Lett.* **2006**, *97*, 146103.
- (81) Abufager, P. N.; Canchaya, J. G. S.; Wang, Y.; Alcamí, M.; Martin, F.; Soria, L. A.; Martiarena, M. L.; Reuter, K.; Busnengo, H. F. Theoretical Study of the Structure of Self-assembled Monolayers of Short Alkylthiolates on Au(111) and Ag(111): The Role of Induced Substrate Reconstruction and Chain–chain Interactions. *Phys. Chem. Chem. Phys.* **2011**, *13*, 9353–9362.
- (82) Otaño, D.; Veening, T.; Brocks, G. Self-Assembled Monolayer Induced Au(111) and Ag(111) Reconstructions: Work Functions and Interface Dipole Formation. *J. Phys. Chem. C* **2012**, *116*, 7826–7837.
- (83) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y. T.; Parikh, A. N.; Nuzzo, R. G. Comparison of the Structures and Wetting Properties of Self-Assembled Monolayers of Normal-Alkanethiols on the Coinage Metal-Surfaces, Cu, Ag, Au. *J. Am. Chem. Soc.* **1991**, *113*, 7152–7167.
- (84) Ratner, B. D.; Castner, D. G. *Surface Analysis—The Principle Techniques*; Wiley & Sons: Chichester, 1997.
- (85) Ludwig, E.; Strunskus, T.; Hellmann, S.; Nefedov, A.; Wöll, C.; Kippa, L.; Rossnagel, K. Electronic Structure, Adsorption Geometry, and Photoswitchability of Azobenzene Layers Adsorbed on Layered Crystals. *Phys. Chem. Chem. Phys.* **2013**, *15*, 20272–20280.
- (86) Kang, J. F.; Ullman, A.; Liao, S.; Jordan, R. Mixed Self-Assembled Monolayers of Highly Polar Rigid Biphenyl Thiols. *Langmuir* **1999**, *15*, 2095–2098.
- (87) Roper, M. G.; Skegg, M. P.; Fisher, C. J.; Lee, J. J.; Dhanak, V. R.; Woodruff, D. P.; Jones, R. G. Atop Adsorption Site of Sulphur Head Groups in Gold-Thiolate Self-Assembled Monolayers. *Chem. Phys. Lett.* **2004**, *389*, 87–91.
- (88) Brete, D.; Przyrembel, D.; Eickhoff, C.; Carley, R.; Freyer, W.; Reuter, K.; Gahl, C.; Weinelt, M. Mixed Self-Assembled Monolayers of Azobenzene Photoswitches with Trifluoromethyl and Cyano End Groups. *J. Phys.: Condens. Matter* **2012**, *24*, 394015.
- (89) Schmidt, R.; Hagen, S.; Brete, D.; Carley, R.; Gahl, C.; Dokic, J.; Saalfrank, P.; Hecht, S.; Tegeder, P.; Weinelt, M. On the Electronic and Geometrical Structure of the Trans- and Cis-Isomer of Tetra-Tert-Butyl-Azobenzene on Au(111). *Phys. Chem. Chem. Phys.* **2010**, *12*, 4488–4497.
- (90) Zharnikov, M.; Küller, A.; Shaporenko, A.; Schmidt, E.; Eck, W. Aromatic Self-Assembled Monolayers on Hydrogenated Silicon. *Langmuir* **2003**, *19*, 4682–4687.
- (91) Ballav, N.; Schüpbach, B.; Dethloff, O.; Feulner, P.; Terfort, A.; Zharnikov, M. Direct Probing Molecular Twist and Tilt in Aromatic Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2007**, *129*, 15416–15417.
- (92) Hamoudi, H.; Kao, P.; Nefedov, A.; Allara, D. L.; Zharnikov, M. X-ray Spectroscopy Characterization of Self-Assembled Monolayers of Nitrile-Substituted Oligo(phenylene ethynylene)s with Variable Chain Length. *Beilstein J. Nanotechnol.* **2012**, *3*, 12–24.
- (93) Ossowski, J.; Wächter, T.; Silies, L.; Kind, M.; Noworolska, A.; Blobner, F.; Gnatek, D.; Rysz, J.; Bolte, M.; Feulner, P.; et al. Thiolate versus Selenolate: Structure, Stability and Charge Transfer Properties. *ACS Nano* **2015**, *9*, 4508–4526.
- (94) Trotter, J. Biphenyl Single Crystal Structure. *Acta Crystallogr.* **1961**, *14*, 1135.
- (95) Cassie, A. B. D.; Baxter, S. Wettability of Porous Surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546–551.
- (96) Drelich, J.; Wilbur, J. L.; Miller, J. D.; Whitesides, G. M. Contact Angles for Liquid Drops at a Model Heterogeneous Surface Consisting of Alternating and Parallel Hydrophobic/Hydrophilic Strips. *Langmuir* **1996**, *12*, 1913–1922.
- (97) Ossowski, J.; Rysz, J.; Krawiec, M.; Maciazek, D.; Postawa, Z.; Terfort, A.; Cyganik, P. Oscillations in the Stability of Consecutive Chemical Bonds Revealed by Ion-Induced Desorption. *Angew. Chem., Int. Ed.* **2015**, *54*, 1336–1340.
- (98) Tarlov, M. J.; Newman, J. G. Static Secondary Ion Mass Spectrometry of Self-Assembled Alkanethiol Monolayers on Gold. *Langmuir* **1992**, *8*, 1398–1405.
- (99) Arezki, B.; Delcorte, A.; Garrison, B. J.; Bertrand, P. Understanding Gold-Thiolate Cluster Emission from Self-assembled Monolayers upon Kilolectronvolt Ion Bombardment. *J. Phys. Chem. B* **2006**, *110*, 6832–6840.
- (100) Leggett, G. J. *TOF-SIMS: Surface Analysis by Mass Spectrometry*; IM Publications LLP: Chichester, 2001.
- (101) McGuinness, C. L.; Shaporenko, A.; Zharnikov, M.; Walker, A.; Allara, D. L. Molecular Self-Assembly at Bare Semiconductor Surfaces: Investigation of the Chemical and Electronic Properties of the Alkanethiolate-GaAs(001) Interface. *J. Phys. Chem. C* **2007**, *111*, 4226–4234.

(102) Wong, S. C. C.; Lockyer, N. P.; Vickerman, J. C. Mechanisms of Secondary Ion Emission from Self-Assembled Monolayers and Multilayers. *Surf. Interface Anal.* **2005**, *37*, 721–730.

(103) Rading, D.; Kersting, R.; Benninghoven, A. Secondary Ion Emission from Molecular Overlayers: Thiols on Gold. *J. Vac. Sci. Technol., A* **2000**, *18*, 312–319.

(104) Harada, J.; Ogawa, K.; Tomoda, S. Molecular Motion and Conformational Interconversion of Azobenzenes in Crystals as Studied by X-ray Diffraction. *Acta Crystallogr., Sect. B: Struct. Sci.* **1997**, *53*, 662–672.

(105) Braun, O. M.; Kivshar, Y. S. Nonlinear Dynamics of the Frenkel-Kontorova Model. *Phys. Rep.* **1998**, *306*, 1–108.

(106) Dauselt, J.; Zhao, J.; Kind, M.; Bashir, A.; Terfort, A.; Zharnikov, M. Compensation of the Odd-Even Effects in Aromatic Self-Assembled Monolayers by Non-Symmetric Attachment of the Aromatic Part. *J. Phys. Chem. C* **2011**, *115*, 2841–2854.

(107) Azzaroni, O.; Vela, M. E.; Andreasen, G.; Carro, P.; Salvarezza, R. C. Electrodesorption Potentials of Self-Assembled Alkanethiolate Monolayers on Ag(111) and Au(111). An Electrochemical, Scanning Tunneling Microscopy and Density Functional Theory Study. *J. Phys. Chem. B* **2002**, *106*, 12267–12273.

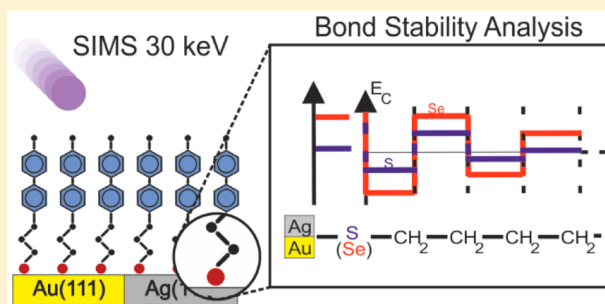
(108) Ito, E.; Ito, H.; Hayashi, T.; Hara, M.; Noh, J. Influence of Surface Morphology and Substrate on Thermal Stability and Desorption Behavior of Octanethiol Self-Assembled Monolayers: Cu, Ag, and Au. *J. Phys. Chem. C* **2012**, *116*, 17586–17593.

(109) Cometto, F. P.; Parades-Olivera, P.; Macagno, V. A.; Patrito, E. M. Density Functional Theory Study of the Adsorption of Alkanethiols on Cu(111), Ag(111), and Au(111) in the Low and High Coverage Regimes. *J. Phys. Chem. B* **2005**, *109*, 21737–21748.

Relative Stability of Thiolate and Selenolate SAMs on Ag(111) Substrate Studied by Static SIMS. Oscillation in Stability of Consecutive Chemical Bonds

Jakub Ossowski,[†] Jakub Rysz,[†] Andreas Terfort,[‡] and Piotr Cyganik^{*,†}[†]Smoluchowski Institute of Physics, Jagiellonian University, Łojasiewicza 11, 30-348 Krakow, Poland[‡]Institut für Anorganische und Analytische Chemie, Universität Frankfurt, Max-von-Laue-Straße 7, 60438 Frankfurt, Germany

ABSTRACT: The stability of chemical bonds at the molecule–metal interface is of fundamental importance for a majority of applications based on organic materials. It remains, however, extremely difficult to determine this stability using experimental and theoretical methods. A detailed analysis of the static SIMS (S-SIMS) data obtained for the homologous series of thiolate- and selenolate-based self-assembled monolayers (SAMs) on the Ag(111) substrate reveals positional oscillations in the stability of consecutive chemical bonds in the vicinity of the molecule–metal interface. The observed oscillations are much more pronounced compared to recently reported analogous data for the Au(111) substrate, which confirms the universal nature of this phenomenon and its strong dependence on the type of molecule binding atom (S or Se) and the substrate (Ag or Au). Importantly, such an analysis has not been conducted to date using any other technique, and this study not only reveals the universal mechanisms of molecule–metal interface stability but also presents S-SIMS as a unique tool for such an analysis.



1. INTRODUCTION

Self-assembled monolayers (SAMs)¹ currently play a key role in many aspects of surface and thin film design, which is related to further progress in different areas of nanotechnology, ranging from patterned materials^{2–5} and molecular electronics^{6–8} to biocompatible^{9–11} materials. To our knowledge, the most basic parameter in the design of SAMs is the stability of their chemical bonding with selected substrates. Unfortunately, it remains extremely difficult to determine this parameter using both experimental analysis and theoretical predictions, which thus limits our efforts in the purposeful design of SAMs. Therefore, new experimental approaches for exploring the molecule–substrate interface stability are urgently required to provide systematic and general observations, which could in turn enable the development of theoretical models. In this work, we demonstrate that static secondary ion mass spectrometry (S-SIMS) can play such a role by not only providing an alternative method for conducting typical stability experiments but, more importantly, revealing and exploring the stability mechanisms which to date has not been analyzed by any other technique.

Over the last 3 decades, S-SIMS has emerged as one of the fundamental surface and elemental characterization tools to study the composition and reactivity, and more recently, for the imaging of organic films and biological structures.^{12–17} An extremely high sensitivity, which enables the trace analysis of the chemical composition down to the ppb level, is one of the key features that make S-SIMS particularly attractive for many applications. Among organic films, SAMs are considered as

model systems for S-SIMS analysis from both the experimental and calculation viewpoint.^{18–28} To address the issue of the S-SIMS sensitivity to the stability of the molecule–metal interface, we have selected a homologous series of hybrid aromatic/aliphatic SAMs in the general form of $\text{CH}_3-(\text{C}_6\text{H}_4)_2-(\text{CH}_2)_n-\text{S}(\text{Se})/\text{Ag}$ ($n = 2–6$), where either the S atom (BPnS) or Se atom (BPnSe) acts as a headgroup binding molecule to the Ag(111) surface (see Figure 1). Previous spectroscopic^{29–33} and microscopic^{34–36} measurements demonstrated that BPnS(Se) molecules form very well-defined SAMs on Au(111) and Ag(111) substrates, which can be considered model systems for systematic studies. In contrast to simple alkanethiols,¹ the structure of this type of SAMs depends strictly on the parity of the parameter n (the number of CH_2 groups). For the Au(111) substrate, this odd–even effect results in a higher packing density of more upright oriented molecules for odd-numbered members of the BPnS(Se)/Au series. In contrast, for the Ag(111) substrate, this odd–even effect is reversed as a consequence of the different value of the substrate-S(Se)-C bond angle that is preferred for the Au(111) and Ag(111) substrates and amounts to $\sim 104^\circ$ and $\sim 180^\circ$, respectively.^{30–33} The impact of this odd–even effect on film stability has only been analyzed for the Au(111) substrate. It was shown that the odd–even effect influences the stability of BPnS/Au SAMs toward electro-

Received: October 25, 2016

Revised: December 6, 2016

Published: December 8, 2016

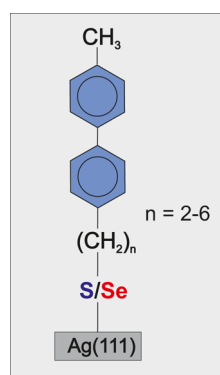


Figure 1. Types of SAMs used in this study. The acronym BP n S(Se)/Ag corresponds to $\text{CH}_3-(\text{C}_6\text{H}_4)_2-(\text{CH}_2)_n-\text{S}(\text{Se})/\text{Ag}(111)$, with $n = 2-6$.

chemical desorption,^{37,38} ion-induced desorption,³⁹ exchange by other molecules,^{40,41} electron irradiation⁴² and thermally induced phase transitions.^{43–45} For all of these odd–even effects, with respect to the different aspects of film stability, the even-numbered members turn out to be less stable than the odd-numbered BP n S(Se)/Au SAMs. However, for the Au(111) substrate, it was also demonstrated that the substitution of the headgroup atom from S to Se has an even more pronounced impact on the film stability in addition to the aforementioned structural odd–even effect. Previous exchange experiments⁴¹ demonstrated a much higher stability of BP n Se/Au SAMs compared to BP n S/Au SAMs due to the stronger Se–Au bond compared to the S–Au bond. Lastly, a recent stability study⁴⁶ for the BP n S/Au SAMs revealed the effect of positional oscillation on the stability of consecutive chemical bonds of adsorbed molecules at the molecule–Au interface. This study indicated that the strength of the chemical bonding with the Au(111) substrate via the S(Se)–Au bond influences the stability of several consecutive chemical bonds inside the chemisorbed molecule. Moreover, our most recent experiments also indicate a direct influence of this oscillation effect on the relative conductivity of thiolate and selenolate SAMs on the Au(111) substrate.⁴⁷

In summary, we note that, to date, the analysis of the molecule–metal interface stability for the model BP n S(Se) SAMs has only been performed for the Au(111) substrate. By current experimental study, we extend this analysis to the Ag(111) substrate and address several important issues. First, we analyze the impact of the odd–even effect on the stability of BP n S(Se)/Ag SAMs. Next, we determine the impact of S $\rightarrow$ Se substitutions on the bonding with the Ag(111) substrate. Finally, and most importantly, we analyze the impact of the Au $\rightarrow$ Ag substrate modification on the effect of positional oscillation in stability of consecutive chemical bonds to confirm the origin of this phenomenon and its universal nature. To enable the direct comparison of all the effects reported here for the Ag(111) substrate with respective data for the Au(111) substrate in a single set of experiments, we have reproduced some of the data obtained earlier for the Au(111) substrate. This combined analysis provides also some implications on the relative thermal stability and conductance of these SAMs and presents S-SIMS as a new and unique tool for the molecule–metal interface stability analysis.

2. EXPERIMENTAL PART

The Ag(111) and Au(111) substrates were prepared by evaporating 150 nm of silver/gold onto single-crystal silicon (100) wafers (ITME, Warsaw) primed with a 5 nm chromium adhesion layer (base pressure of $\sim 10^{-7}$ mbar, rate 0.1 nm/s). The synthesis of the BP n SH ($\text{CH}_3(\text{C}_6\text{H}_4)_2(\text{CH}_2)_n\text{SH}$, $n = 2-6$) molecules has been described elsewhere.³¹ The precursor molecules for the fabrication of the BP n Se SAMs were diselenides (BP n Se–SeBP n : $\text{CH}_3(\text{C}_6\text{H}_4)_2(\text{CH}_2)_n\text{Se}-(\text{CH}_2)_n(\text{C}_6\text{H}_4)_2\text{CH}_3$, $n = 2-6$), whose synthesis has been described elsewhere.⁴⁸ HDT ($\text{CH}_3(\text{CH}_2)_{15}\text{SH}$) was used as received from Aldrich. The HDSe molecules were obtained by the reduction of a hexadecyldiselenide/-triselenide mixture with lithium aluminum hydride. The BP n S(Se)/Ag(Au) SAMs were prepared by immersing the substrate (Ag or Au), directly after the evaporation process was completed, into 0.1 mM solutions of the respective precursors in ethanol at room temperature for 24 h. After immersion, the samples were rinsed with pure ethanol, blow-dried with nitrogen and immediately transferred to the experimental setup (S-SIMS or IRRAS). For exchange experiments, the BP n S(Se) SAMs were immersed in 1 mM ethanolic solutions of HDT or HDSe for 24 h.

Infrared reflection–absorption spectroscopy (IRRAS) measurements were performed with a dry-air-purged Thermo Scientific Nicolet 6700 FTIR spectrometer model equipped with a liquid nitrogen-cooled MCT detector. All spectra were taken using p-polarized light incident at a fixed angle of 80° with respect to the surface normal. Spectra were measured at a resolution of 2 cm^{-1} and are reported in absorbance units $A = -\log R/R_0$, where R is the reflectivity of the substrate with a monolayer and R_0 is the reflectivity of the reference. Substrates covered with perdeuterated hexadecanethiolate SAMs were used as the reference samples.

The SIMS analysis was performed using a TOF SIMS V system (ION TOF GmbH, Germany). The instrument was operated at a base pressure of 6×10^{-10} mbar. The primary 30 keV Bi^+ ion beam was scanned over a $500\text{ }\mu\text{m} \times 500\text{ }\mu\text{m}$ area during data acquisition. All spectra were acquired in the static SIMS regime (S-SIMS) using a total ion dose of up to 5×10^{10} ions/ cm^2 , which for this type of SAM ensures an analysis with no ion-induced damage, as documented by our previous studies.⁴⁹ The secondary positive or negative ions were extracted into a reflectron-equipped time-of-flight mass spectrometer before they reached the MCP detector. For each type of BP n S(Se)/Ag(Au) SAM, three different samples were prepared and six different areas (three for positive spectra and three for negative spectra in the range up to $m/z = 800$) on each sample were examined, resulting in ca. 10% reproducibility in the peak intensities. Before the analysis, all spectra were normalized to the respective total number of counts.

3. RESULTS

Two types of experiments have been performed in this study. The first experiments, which probe the relative stability of the BP n S/Ag and BP n Se/Ag SAMs toward exchange by other molecules that are capable of forming SAMs, were conducted and compared with corresponding data obtained for the Au substrate. In the second experiment, which was the primary part of this study, the ion-induced desorption of the BP n S(Se)/Ag SAMs was determined via S-SIMS analysis and compared with corresponding data obtained for the Au substrate.

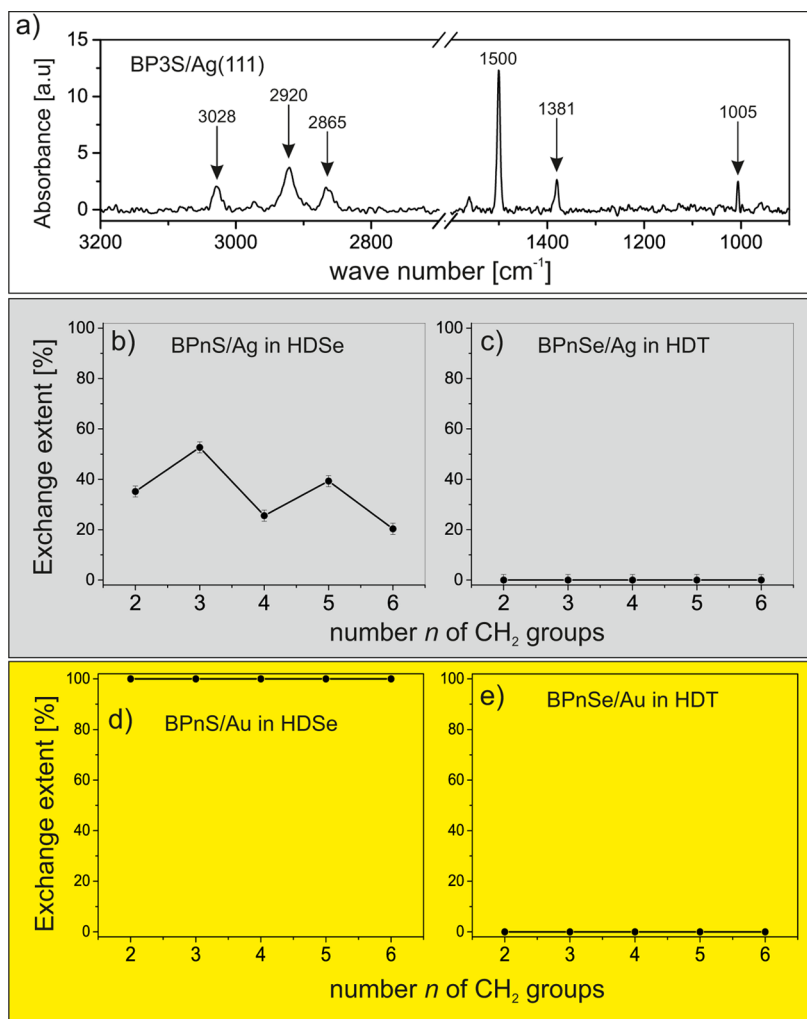


Figure 2. Analysis of exchange experiments by IRRAS data. Panel a is an example of the IRRAS spectrum for the BP3S/Ag with the characteristic absorption bands indicated (see the text for details). In the middle panels (b, c), the relative exchange extent for the BPnS(Se)/Ag after a 24 h incubation in 1 mM HDSe (b) or HDT (c) ethanolic solution at room temperature is presented as a function of the parameter *n*. In the lower panels (d, e), the corresponding data for the BPnS(Se)/Au SAMs are presented. See the text for more details.

3.1. Exchange Experiments. To probe the relative stability of S–Ag and Se–Ag bonds in the exchange experiments, a 24 h incubation of the BPnS/Ag and BPnSe/Ag samples in 1 mM hexadecaneselenol (HDSe) or hexadecanethiol (HDT) ethanolic solution, respectively, was performed. The progress of the exchange reaction was monitored by IRRAS. As a reference for monitoring the exchange process, the IRRAS analysis for the native BPnS(Se)/Ag (*n* = 2–6) SAMs was first performed. Several absorption bands characteristic of this type of SAM could be identified, as indicated in Figure 2a, where an example of the spectrum obtained for the BP3S/Ag SAM is presented. According to previous detailed spectroscopic experiments,^{31,33} the biphenyl part of the molecules results in bands at ~ 3028 (C–H stretching), ~ 1500 (C–C stretching), and ~ 1005 cm^{−1} (C–H bending), whereas the aliphatic part is attributed to bands located at ~ 2920 (C–H asymmetric stretching) and ~ 2865 cm^{−1} (C–H symmetric stretching). The weak band observed at ~ 1380 cm^{−1} corresponds to the C–CH₃ symmetric deformation at the terminal group. Following the methodology proposed in our previous study,⁴¹ we calculated the exchange percentage of a given BPnS(Se)/Ag SAM by taking the total intensity of the bands exclusively related to the biphenyl moiety

(i.e., ~ 3028 , ~ 1500 , and ~ 1005 cm^{−1}) and normalizing it by the respective value obtained for the native sample. The results obtained after a 24 h incubation of BPnS/Ag (*n* = 2–6) SAMs in a 1 mM ethanolic solution of HDSe are presented in Figure 2b and show an odd–even dependence with a higher exchange percentage for odd-numbered members of the BPnS/Ag series. In contrast, the experiments presented in Figure 2c for the corresponding BPnSe/Ag (*n* = 2–6) SAMs exchanged in a 1 mM ethanolic solution of HDT show no exchange at all. For comparison, in Figure 2d and 2e, the corresponding experiments performed for the Au substrate show a complete exchange for the BPnS/Au SAMs and no exchange for the BPnSe/Au SAMs, which is in full agreement with our previous study.⁴¹

3.2. S-SIMS Experiments. S-SIMS experiments were performed for four homologous series of BPnS(Se)/Ag(Au) SAMs with *n* = 2–6 to independently probe the impact of the headgroup atom (S or Se) and the substrate (Ag or Au) modification on the molecule–metal interface stability. First, the signal of the molecule–metal cluster ions, which are very well-known fingerprints used in the S-SIMS technique to determine the formation of SAMs,^{18–27} was analyzed. Such an analysis of the molecule–metal clusters ions for both

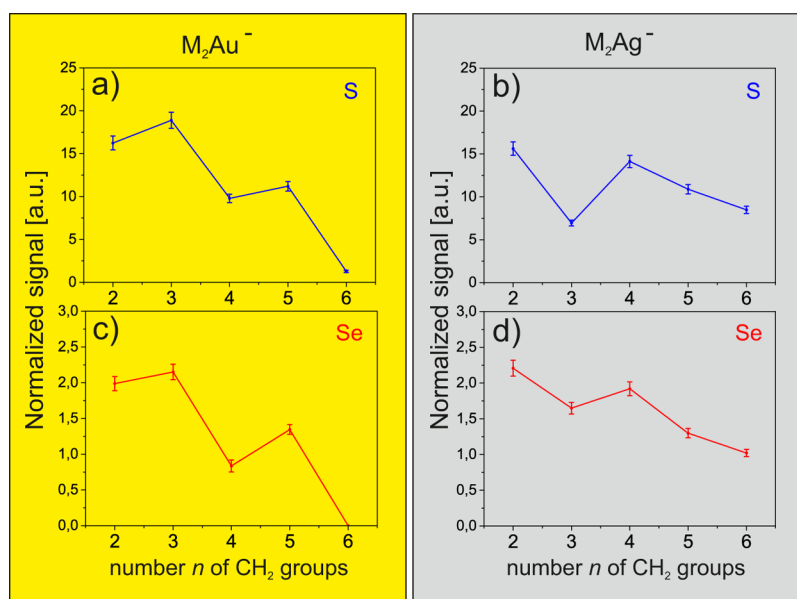


Figure 3. S-SIMS data analysis. Left and right panels show the normalized signal of the $[(M_2Au)^-]$ and $[(M_2Ag)^-]$ emission, respectively. (a and b) Emission from $BPnS/Au$ and $BPnS/Ag$ SAMs, respectively (blue line). (c and d) Emission from $BPnSe/Au$ and $BPnSe/Ag$ SAMs, respectively (red line). See the text for more details.

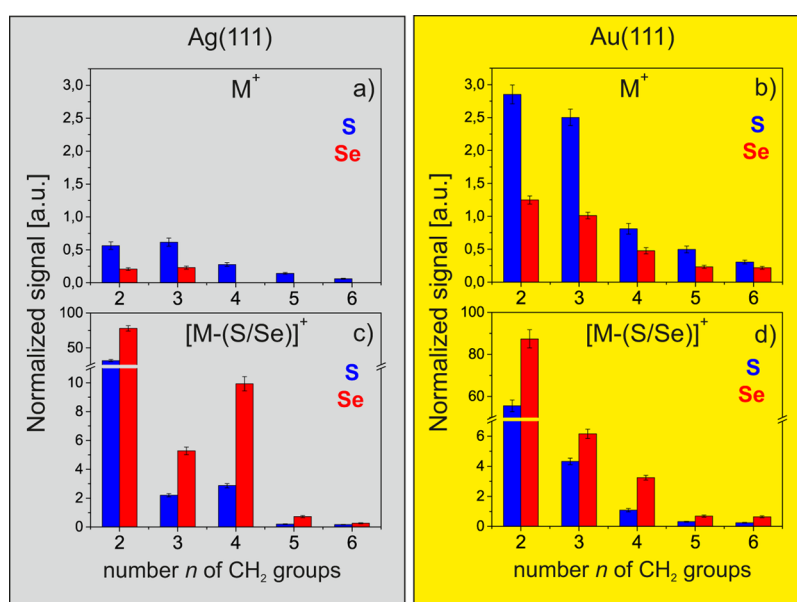


Figure 4. S-SIMS data analysis. Left and right panels show data obtained for $BPnS(Se)/Ag$ and $BPnS(Se)/Au$, respectively. (a and b) Normalized emission of ions related to the complete molecule $[M]^+$ emitted from $BPnS(Se)/Ag$ and $BPnS(Se)/Au$, respectively. (c and d) Normalized emission of ions related to the desulfurized or deselenized molecule $[M-(S/Se)]^+$ emitted from $BPnS(Se)/Ag$ and $BPnS(Se)/Au$, respectively. Data obtained for the S and Se headgroup atoms are presented in blue and red bars, respectively. See the text for more details.

$BPnS(Se)/Ag$ and $BPnS(Se)/Au$ SAMs was performed for the first time. An example of the obtained data is shown in Figure 3, where the normalized signal (normalized to the total number of counts) of the negative M_2Au^- and M_2Ag^- secondary ions is presented. The symbol “M” denotes the respective molecule in the general form of $CH_3(C_6H_4)_2(CH_2)_nS(Se)$ with $n = 2–6$. The data obtained for the Ag and Au substrate are similar and exhibit two common features. First, independent of the type of substrate, the intensity of the $M_2Ag(Au)^-$ signal is about an order of magnitude higher for the S headgroup ($BPnS$) compared to the corresponding Se headgroup ($BPnSe$). Second, depending on the parameter n for both types of

substrates (Ag and Au) and headgroup atoms (S and Se), a much weaker but visible odd–even variation of the signal intensity is observed. Importantly, the phase of these odd–even oscillations for both the S- and Se-based SAMs is reversed for the Ag and Au substrates. For the Ag substrate, a higher intensity of the M_2Ag^- signal is observed for even-numbered members of the $BPnS(Se)$ series with the exception of the $BP6S(Se)/Ag$ SAMs, for which the signal is lower than expected. This could, however, be the result of a general drop in the secondary ion signal with the increase in the mass of analyzed ion, which also explains why for the Au substrate,

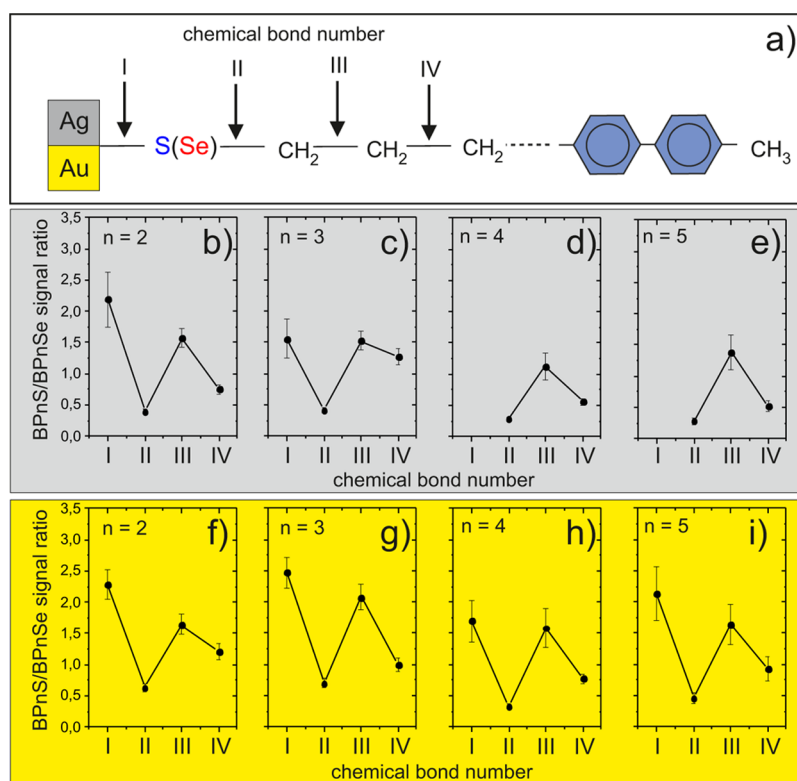


Figure 5. S-SIMS data analysis. In part a, the schematic location of the four consecutive chemical bonds probed in the experiment is presented. The emission of M^+ , $[M - S(Se)]^+$, $[M - CH_2S(Se)]^+$ and $[M - CH_2CH_2S(Se)]^+$ secondary ions corresponds to the scission of bond I, II, III, and IV, respectively. In panels b–e, the relative intensities of the positive ions emitted from the BPnS/Ag and BPnSe/Ag SAMs for $n = 2$ (b), $n = 3$ (c), $n = 4$ (d), and $n = 5$ (e) correspond to the scission of the indicated bonds I–IV. In panels f–i, a corresponding analysis for identical positive ions emitted from the BPnS/Au and BPnSe/Au SAMs is shown. See the text for more details.

where the phase of this oscillation is reversed, the BP6S/Au and BP6Se/Au SAMs show an approximately zero intensity.

In the next step, the emission of positive ions that correspond to the complete molecule $M_{S/Se}^+$ and its desulfurized ($[M - S]^+$) or deselenized ($[M - Se]^+$) fragments was analyzed. The respective data are presented in Figure 4. For the Ag substrate, the emission of $M_{S/Se}^+$ ion has a very low intensity, but it is systematically more efficient for the S headgroup compared to the Se headgroup (Figure 4a). Corresponding data obtained for the Au substrate show a much higher level of the $M_{S/Se}^+$ ion emission compared with the Ag substrate (Figure 4b), but similar to the Ag substrate, a higher intensity of the $M_{S/Se}^+$ ion emission is observed for the S headgroup compared to Se headgroup. The emission of the desulfurized ($[M - S]^+$) and deselenized ($[M - Se]^+$) fragments was efficient for both the Ag and Au substrates, as shown in Figures 4c and 4d, respectively. Importantly, in contrast to the data obtained for the $M_{S/Se}^+$ ion, the emission of $[M - S]^+$ and $[M - Se]^+$ ions is systematically more efficient for the Se headgroup compared to the S headgroup. Additionally, whereas for the Au substrate, only a systematic drop in the $[M - S]^+$ and $[M - Se]^+$ intensity is observed as the length of molecules (defined by the parameter n) increases, for the Ag substrate an odd–even variation of this signal is also observed along with a higher emission for even numbered members of the BPnS(Se)/Ag series.

The emission of $M_{S/Se}^+$ and $[M - S(Se)]^+$ secondary ions results from the ion-beam induced scission of the first and the second chemical bond along the molecular chain of the adsorbed molecule, respectively. For both substrates, the

emission shows a reversed relationship for the S and Se headgroup atoms; i.e., for S, a higher emission of $M_{S/Se}^+$ with a simultaneous lower emission of $[M - S(Se)]^+$ is observed compared to the Se analogue. In Figure 5, a broader analysis of this effect is shown by comparing the relative intensity of the secondary ions emitted from the S and Se analogues, which correspond to molecular fragments generated by the scission of one of four consecutive chemical bonds along the molecular chain; the consecutive bonds start from the headgroup atom and are numbered as bonds I–IV (as shown in the schematic cartoon in Figure 5a). The data obtained for the BPnS(Se)/Ag SAMs with $n = 2, 3, 4$, and 5 (the low intensity of the respective signals for $n = 6$ precludes such an analysis) are presented in Figure 5b–e. The corresponding data obtained for the BPnS(Se)/Au SAMs are presented in Figure 5f–i. We note that for $n = 4$ and $n = 5$ for the BPnS(Se)/Ag SAMs, the signal ratio for bond number I is missing (the absence of corresponding points in Figure 5d and 5e). This is due to the lack of a measurable emission level of the complete molecule in this case (see Figure 4a) and thus, a high ($\gg 1$), but undefined at this point, value of the corresponding ratio of this signal for the S- and Se-based analogues.

The final data analysis step is presented in Figure 6. In panel a, the analysis of the $[C_{15}H_{15}]^+$ secondary ion emission from the BPnS(Se)/Ag(Au) SAMs is summarized. The schematic cartoon in this panel shows that the emission of this particular fragment from the BPnS(Se)/Ag(Au) series (with $n = 2$ – 6) requires the cleavage of consecutive chemical bonds along the aliphatic chain, i.e., for $n = 2$, the S(Se)–C¹ bond has to be cleaved, for $n = 3$ the C¹–C² bond has to be cleaved, etc. (the

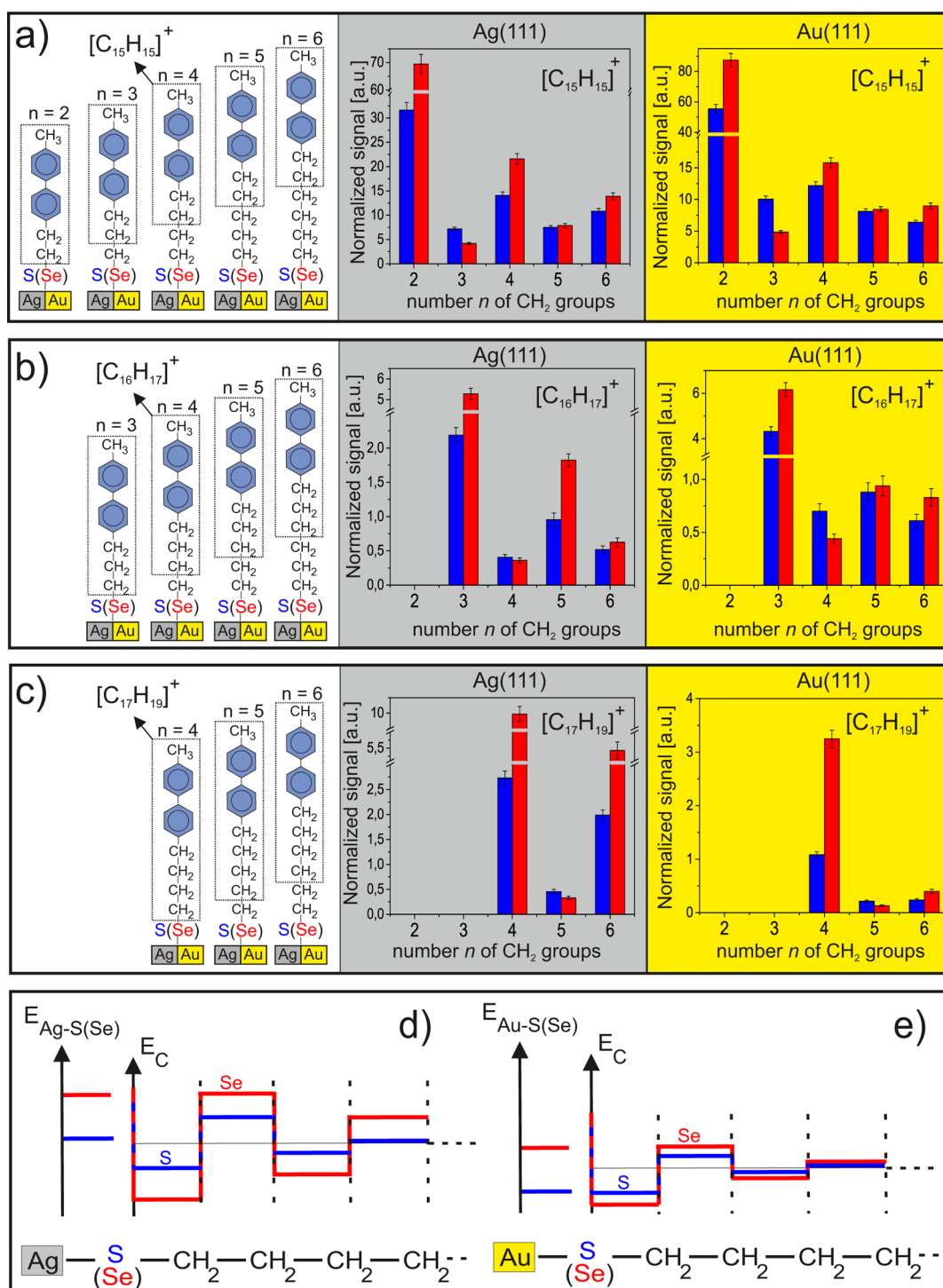


Figure 6. S-SIMS data analysis. Panel a shows the normalized signal of the $[C_{15}H_{15}]^+$ emission for BPnS/Ag (blue bars) and BPnSe/Ag (red bars) and the corresponding signals for BPnS/Au and BPnSe/Au. Panels b and c show the respective data for the $[C_{16}H_{17}]^+$ and $[C_{17}H_{19}]^+$ emissions. The white boxes in the schemes on the left side of panels (a)–(d) indicate the part of the molecule that corresponds to a specific type of secondary ion, and they also indicate the location of the bond scission, which results in the emission. Note that the phase of this odd–even effect remains the same for the BPnS(Se)/Au and BPnS(Se)/Ag SAMs, and therefore, this odd–even effect is *not* a consequence of the known structural odd–even effect of these SAMs (see the text for details). Panels d and e schematically summarize the S-SIMS results for the Ag(111) and Au(111) substrates: (i) the higher bond energy of Se–Au(Ag) compared to S–Au(Ag), (ii) the higher bond energy of S(Se)–Ag compared to S(Se)–Au, (iii) the oscillations in the bond energies of the consecutive chemical bonds along the backbone of the molecule, (iv) the oscillation effect diminishes with increasing distance from the molecule–metal interface, and (v) the amplitude of the oscillations for the selenium-based SAMs on both types of substrates is higher, and independently, the amplitude is higher for the Ag substrate for both types of head groups.

upper indexes “1” and “2” denote the first and second C atom, respectively, of the aliphatic chain, counting from the headgroup atom attachment to the chain). The data

summarized in this panel show a few extremely interesting features. First, the intensity of the $[C_{15}H_{15}]^+$ emission depends strongly on the parameter n , with oscillations observed for both

the S and Se analogues on the Au and Ag substrates and a higher signal for even values of n . Second, the same phase of these oscillations is observed for the S and Se analogues, which is also independent of the type of substrate (Ag or Au). Third, the amplitude of these oscillations for both types of substrates is higher for the Se analogues compared to the S analogues. Fourth, the oscillation amplitude rapidly diminishes as the number n increases for both types of headgroup atoms (S and Se) and substrates (Ag and Au). Fifth, the amplitude of these oscillations is systematically higher for the Ag substrate compared to the Au substrate. In panels b and c, the same analysis was performed for the $[C_{16}H_{17}]^+$ and $[C_{17}H_{19}]^+$ fragments, respectively. As schematically indicated in the respective cartoons, the analysis in these cases is limited to the BPnS(Se)/Ag(Au) SAMs with $n = 3-6$ for $[C_{16}H_{17}]^+$ and $n = 4-6$ for $[C_{17}H_{19}]^+$ due to the increased length of the analyzed fragments. We note here that for the $[C_{16}H_{17}]^+$ fragment, the phase of signal oscillation with n is reversed compared to the data obtained for the $[C_{15}H_{15}]^+$ fragment. This is a consequence of shifting our analysis from $n = 2-6$ to $n = 3-6$, i.e., correlating the termination of the first analyzed Ag(Au)–S(Se) bond with $n = 3$ for the emission of the $[C_{16}H_{17}]^+$ fragment instead of $n = 2$ for the emission of the $[C_{15}H_{15}]^+$ fragment. Accordingly, the phase of signal oscillation for the $[C_{17}H_{19}]^+$ fragment remains the same as that for the $[C_{15}H_{15}]^+$ fragment because the termination of the first analyzed Ag(Au)–S(Se) bond is correlated with $n = 4$, i.e., shifting this value by 2 in comparison to $n = 2$ for the $[C_{15}H_{15}]^+$ fragment. Importantly, all the observations mentioned above for the $[C_{15}H_{15}]^+$ emission are fully reproduced in the data obtained for the $[C_{16}H_{17}]^+$ and $[C_{17}H_{19}]^+$ fragments, i.e., the oscillation amplitude rapidly diminishes with an increasing number n , and it is clearly higher for the Se analogues and independently higher for the Ag substrate.

4. DISCUSSION

We start the discussion with the analysis of the exchange experiments, which resulted in two important observations. First, for both types of substrates (Ag and Au), the selenol-based BPnSe/Ag(Au) SAMs are fully resistant (within our experimental conditions) to exchange by hexadecanethiol (HDT) molecules; simultaneously, the thiol-based BPnS/Ag(Au) SAMs show significant exchange by the hexadecaneselenol (HDSe) molecules for the Ag substrate and a complete exchange by the hexadecaneselenol (HDSe) molecules for the Au substrate. This observation demonstrates a much higher stability of Se-based SAMs compared to their S-based analogues on both Ag and Au substrates. Because the chemical bond, which links the molecule of the original SAM to the respective substrate, has to be cleaved during the exchange process, we conclude that this stability difference in the exchange process results from a significantly higher stability of the Se–Ag(Au) bond compared to the S–Ag(Au) bond in this type of SAM. A higher stability of the Se–Au bond compared to the S–Au bond has been previously reported in similar exchange experiments for BPnS(Se) SAMs⁴¹ and has very recently been reported for purely aromatic SAMs based on naphthalene precursors.⁴⁷ For the Ag substrate, previous competitive adsorption experiments for phenyl-based SAMs concluded that there was a higher stability for S-based SAMs compared to the Se analogues.⁵⁰ These conclusions are inconsistent with the data presented in Figure 2, which indicate the higher stability of Se-based systems on the Ag substrate compared to their S

analogue. Such a discrepancy may result from the particular SAMs and sample preparation procedures used for stability comparisons in previous experiments.⁵⁰ We would like to stress that, in our opinion, for a meaningful comparison of the relative molecule–substrate binding stability, the compared SAMs should not only have the same carbon backbones but also form ordered structures with the same or a very similar molecular packing. Only under such conditions can the contribution of the intermolecular interactions on the stability of analogue films be minimized to determine the role of the molecule–substrate bonding on film stability. Spectroscopic characterization of phenyl-based S and Se SAMs on the Ag substrate, as analyzed in a previous study,⁵⁰ did not address their relative packing density but indicates a different orientation of the molecules with respect to the Ag substrate in the compared SAMs. We also note that previous competitive adsorption experiments were conducted using Ag powder as the substrate, i.e., a very defected and crystallographically undefined substrate, which resulted in a highly defected structure of the respective SAM. Therefore, it is relatively difficult to determine, at this point, to what extent the more efficient absorption of phenyl thiol compared to the selenol analogues was related to (i) the stability of chemical bonding with the substrate via the S–Ag bond, (ii) the interaction of phenyl rings within the monolayer and with the Ag substrate, or simply (iii) the concentration of defects in a given SAM. In contrast, the current analysis is conducted for BPnS(Se)/Ag ($n = 2-6$) SAMs, which have been formed on well-defined Ag(111) substrates and characterized spectroscopically in detail to demonstrate a similar packing density and orientation of molecules in all the compared SAMs. Therefore, in our opinion, the presented exchange data better justifies the correlation between the observed stability differences and the relative strength of the S–Ag and Se–Ag chemical bonding in these SAMs. In particular, the stability analysis presented here is not limited to comparing only two SAMs, instead, two homologous series of analogue SAMs can be compared, which makes the related observations significantly more general.

Current exchange experiments also reveal an odd–even effect in the exchange of BPnS/Ag SAMs by HDSe molecules (Figure 2b). Although a similar effect could not be observed for the BPnS/Au SAMs exchanged by HDSe molecules due to the complete exchange observed in this case (Figure 2d), such an odd–even effect in the exchange was observed for the BPnS/Au SAMs in our previous experiments when HDT molecules were exchanged instead of HDSe molecules (see Figure 5 in ref 41). More importantly, by comparing both exchange experiments performed for the same SAMs on Ag and Au substrates, we conclude that the phase of this effect is reversed upon changing the substrate from Ag to Au. As indicated in the introduction, previous microscopic and spectroscopic characterizations of BPnS(Se)/Ag(Au) SAMs demonstrated that structural odd–even effect also reverses in phase upon changing the substrate from Ag to Au. Thus, the exchange experiment remains fully correlated with the structural odd–even effect.

For a detailed analysis of the observed differences in the stability of the SAMs at the molecule–metal interface, ion-induced desorption experiments have been performed. The emission of secondary ions measured by the S-SIMS results from a convolution of the desorption and ionization processes, which are induced by the impact of primary Bi^+ ions. Two types of characteristic secondary ions were analyzed in our study: molecule–metal clusters and different molecular fragments.

Generally, two different mechanisms of ion-induced desorption of SAMs have been identified in previous studies.^{22,28,39,51–53} The first mechanism is based on the well-known collision cascade process, which develops in the substrate upon primary ion impact and leads to momentum transfer to the surface atoms of the substrate and subsequently, to the desorption of the organic monolayer. In the second so-called chemical reaction mechanism, the desorption of molecular ions is caused by a “gentle” cleavage of chemical bonds (with no significant momentum transfer) within the organic layer by chemical reactions. These reactions are initiated by the reactive fragments (e.g., radicals) created in the organic film as a result of the impact of primary ions. The experimental analysis of the kinetic energy distribution for neutral species demonstrated that majority of the molecular fragments are emitted from SAMs by the chemical reaction mechanism and only a minority by the collision cascade process.^{39,51–53} However, by considering the ionization process, which is essential in the emission analyzed by S-SIMS, we expect that both emission mechanisms must be considered in the emission of molecular fragments.⁴⁶ In contrast, for molecule–metal clusters, the gentle chemical reaction mechanism can be excluded given the presence of metal substrate atoms in the cluster, which have to be emitted by significant momentum transfer, i.e., via the collision cascade mechanism.

We begin the discussion of the S-SIMS data with the M_2Ag^- and M_2Au^- secondary ions, which represent the molecule–metal cluster emission. The emission of these secondary ions is closely correlated to the exchange experiments. First, similar to the exchange experiments, it shows that the selection of the headgroup atom (S or Se) has the highest impact on the intensity of the S-SIMS signal. Specifically, an order of magnitude higher emission of M_2Ag^- and M_2Au^- is observed for the S headgroup atom compared to Se. This extremely strong effect in the S-SIMS data can be correlated with the zero-one effect in the exchange data, which indicate higher stability of the Se–Ag(Au) bonding compared to the S–Ag(Au). As previously indicated, we may assume that the process that leads to the emission of molecule–metal clusters is essentially directed by the collision cascade mechanism. This observation gives us some insight into possible scenarios that result in the emission of molecule–metal clusters based on the molecular dynamics (MD) calculations of the ion-induced desorption process, which are limited to ballistic collisions, i.e., electronic excitations and chemical reactions are not considered in this approach. Such MD simulations, performed for octanethiol SAMs on the Au(111) substrate and used to address the mechanism of molecule–metal cluster formation, demonstrated that M_2Au clusters are formed by two neighboring molecules in the original SAM structure with an Au atom originating from the top surface layer and located in the vicinity of both molecules.²³ Moreover, we note, at this point, that current structural models^{54–56} for the adsorption of thiols on Ag(111) and Au(111) substrates assume that two neighboring molecules bind to the same surface adatom, which directly supports the correlation between the emission of the M_2Ag^- and M_2Au^- ions and the original SAM structure, i.e., the molecule–metal cluster formation is directly correlated with the distance between neighboring molecules and their binding (configuration and strength) with the substrate atoms. The second and less pronounced effect that is observed in the M_2Ag^- and M_2Au^- emission from the BPnS(Se)/Au(Ag) SAMs is the odd–even dependence. Importantly, the phase of

this effect is independent of whether S or Se is used as the headgroup atom, but it becomes reversed once the substrate is changed from the Au(111) to the Ag(111) substrate. Thus, the odd–even effect in M_2Ag^- and M_2Au^- emission is fully correlated to the odd–even effect in the exchange experiments and structural changes in the BPnS(Se)/Au(Ag) SAMs discussed above.

So far, we have discussed the S-SIMS data, which follow changes in the molecule–metal interface stability that were already analyzed by the exchange experiments. In the following part of our discussion, we would like to focus on the molecule–metal interface analysis, which at this moment seems exclusively possible by this technique. Our analysis follows a very recent study⁴⁶ where the S-SIMS data obtained for BPnS(Se)/Au were used to detect the positional oscillations in the stability of consecutive bonds along the adsorbed molecule. By performing a similar analysis for both the Ag and Au substrates, we aimed to determine the universal nature of the model proposed by us to explain this phenomenon and probe its independence on the structural odd–even effect. The first step in this analysis involved comparing the emission of ions that correspond to the complete parent molecule ($M_{S/Se}^+$) for both types of headgroup atoms (S and Se) and substrates (Ag and Au). Our data demonstrate that for both types of substrates, the emission of $M_{S/Se}^+$ is much more pronounced for the S-based monolayers than the Se analogue. Because the emission of these ions results from the ion-beam induced scission of the respective chemical bond linking molecule to the metal substrate, we conclude that irrespective of the Au or Ag substrate, such a bond scission is more efficient for the S headgroup atom. By assuming that the efficiency in terminating a particular chemical bond by ion-induced processes depends on the stability of this bond, as concluded in our recent study based on corresponding experiments, MD simulations, and DFT calculations,⁴⁶ our present results indicate that the stability of the Au(Ag)–Se bond is higher than that of the Au(Ag)–S bond, in this type of SAMs. Importantly, this conclusion is fully consistent with the exchange experiments discussed above for both types of substrate and with the analysis of the M_2Ag^- and M_2Au^- cluster ion emission. In addition, much lower intensity of $M_{S/Se}^+$ ions emission for the Ag substrate compared to Au indicates higher stability of the molecule–metal binding for the latter case.

In the next step of our analysis, the relative emission of the desulfurized $[M - S]^+$ and deselenized $[M - Se]^+$ fragments for both types of substrates was compared (Figure 4). Because the emission of these fragments corresponds to the scission of the S(Se)– C^1 bond, the higher emission observed for the Se-based monolayers on Ag and Au substrates indicates the lower stability of the Se– C^1 bond compared to that of the S– C^1 bond for both types of substrates. From the supporting observation of positional oscillations in the stability of chemical bonds,⁴⁶ such a behavior could be attributed to the fact that valence electrons of the headgroup atom (S or Se) are involved in bonding with the substrate (Ag or Au) atom(s) on one side and with its neighboring C^1 atom on the other side. The increased involvement of valence electrons of the headgroup atom in one of these chemical bonds, i.e., Au(Ag)–S(Se), should result in a lower involvement of these electrons in the second bond, which consequently reduces the stability of the S(Se)– C^1 bond.

In addition to the strong impact of the S or Se headgroup atom on the relative intensity in the emission of $M_{S/Se}^+$ and $[M - S(Se)]^+$ secondary ions, as discussed above, the modification

of this signal with the odd–even change of parameter n is also visible; however, this only occurs for the Ag substrate. Such an effect is pronounced for the $[M - S(\text{Se})]^+$ fragment (Figure 4d) where a higher emission is observed for even numbered members of the BPnS(Se)/Ag series. Here, we indicate that this odd–even variation in the signal is overlaid with a rapid drop of the signal as the n value increases due to an increased mass of the respective molecule. This is the reason why the intensity for $n = 6$ is extremely low and out of sync with this odd–even trend. For the $M_{\text{S/Se}}^+$ ion, where the overall emission is extremely weak, this effect is much less pronounced but still visible for $n = 2, 3$, and 4, with the highest emission observed for $n = 3$, i.e., for the odd-numbered member of the BPnS(Se)/Ag series. Importantly, the higher emission of the $M_{\text{S/Se}}^+$ for the odd-numbered BPnS(Se)/Ag SAMs correlates with the respective exchange experiments that show the lower Ag–S bond stability of odd-numbered members of the BPnS/Ag series (as presented in Figure 2b). Considering that a lower involvement in the Ag–S(Se) bonding should be compensated by a higher involvement in the S(Se)–C¹ bond, one should also observe an odd–even variation in the S(Se)–C¹ bond stability but one that is reversed in phase compared to the Ag–S(Se) bond. This scenario is fully confirmed by the odd–even emission of the $[M - S(\text{Se})]^+$ fragment, which shows lower emission, i.e., higher stability of the S(Se)–C¹ bond, for odd-numbered members of the BPnS(Se)/Ag series. The fact that such an odd–even effect is not observed in the respective data obtained for the Au substrate indicates that the odd–even effect on film stability is less pronounced for the Au substrate than the Ag substrate.

To summarize the discussion above, the increase in the stability of the Ag(Au)–S(Se) bond caused by the change of the binding atom from S to Se or, to a much lower extent, by the odd–even change within the BPnS(Se) series causes a reduction in the Se–C¹ bond stability. The reduction in the Se–C¹ bond stability results, in turn, in a shift of the valence electrons of the C¹ atom toward the C² atom, which leads to an increased strength of the C¹–C² bond, and so on. Following the previous DFT calculations,⁴⁶ this effect should lead, in principle, to the oscillation in the relative stability of consecutive chemical bonds within the aliphatic chain for the S and Se SAMs on both Ag(111) and Au(111) substrates. The amplitude of these oscillations should decrease for consecutive bonds because the disturbances introduced into the electronic structure of the aliphatic chain by chemical bonding to the substrate via the headgroup atom become diminished at larger distances from the molecule–substrate interface: the dislocation of the valence electrons becomes increasingly smaller. Such a prediction is confirmed by the data shown in Figure 5, which analyzes the emission ratio of fragments emitted from S- and Se-based SAMs as a result of the termination of four consecutive chemical bonds (see the schematic illustration in Figure 5a). Importantly, the effect of this oscillation for both Au(111) and Ag(111) substrates has the same phase, which is mutually consistent with the fact a higher bonding strength was observed for Se-based compounds for both types of substrates; therefore, if our explanation of this effect is correct, this defines the common phase of these oscillations. In addition, the amplitude of these oscillations for both types of substrates reduces as the number of consecutive chemical bonds increases, thereby supporting the proposed model.

There is, however, an alternative explanation of the oscillations presented in Figure 5 that we have to consider.

In the current analysis of the data shown in Figure 5, we correlate the stability of consecutive chemical bonds in these SAMs with the emission efficiency of molecular fragments with (importantly) different lengths. One could, therefore, speculate that the observed oscillations in the relative intensity of this emission actually reflects an odd–even mechanism in the ionization efficiency that depends on the length of the emitted fragment, and thus the observed effect is not related to the stability of the respective chemical bonds, as proposed in the model above. To exclude such a hypothesis, further observation of this phenomenon was conducted by analyzing the $[\text{C}_{15}\text{H}_{15}]^+$ molecular fragment emission from the series of BPnS(Se)/Au(Ag) SAMs, i.e., without changing the mass of the analyzed fragment (Figure 6). As indicated in the previous section, a few crucial observations can be made at this point. First, the phase of the oscillations is independent of the type of the headgroup atom, which shows that both types of headgroup atoms give a binding energy of the S(Se)–C¹ bond that is below the typical C^{*n*}–C^{*n*+1} bond energy in long aliphatic chain; thus, this induces the same phase of oscillations in the binding energy of consecutive C–C bonds that propagate from the metal–molecule interface, where the disturbance occurs, into the middle of the molecular chain (see the schematic illustration in Figure 6d). Second, for both head groups, the amplitude of these oscillations vanishes quickly from the interface into the middle of the aliphatic chain, in accordance with the model proposed above. Third, the amplitude of these oscillations is significantly higher for the Se headgroup atom, in accordance with the lower stability of the Se–C¹ bond compared to the S–C¹ bond and thus, the higher stimulation for oscillations in the binding energy of consecutive chemical bonds for the Se headgroup atom. Fourth, the effect is very similar for both Ag and Au substrates, but a higher amplitude of the observed oscillations is noticed in the latter case, which indicates a higher binding energy of S and Se headgroup atoms with the Ag substrate compared to the Au substrate. For the S headgroup, this experimental observation is consistent with previous DFT calculations that predict a higher stability of the Ag–S bonding compared to the Au–S bonding for short alkanethiols on Au and Ag substrates.^{56,57} The common phase of oscillations shown in Figure 6a for the Au and the Ag substrates proves that the observed oscillation effect in the $[\text{C}_{15}\text{H}_{15}]^+$ emission is not related to the odd–even structural effect in the BPnS(Se)/Au(Ag) SAMs because in such a case, the phase of this effect would be reversed upon changing the substrate from Ag → Au.

To confirm that all the above analysis, conducted for the emission of the $[\text{C}_{15}\text{H}_{15}]^+$ fragment, has a very general nature that is not dependent on a particular fragment, a fully analogical analysis has been subsequently performed for the emission of the $[\text{C}_{16}\text{H}_{17}]^+$ and $[\text{C}_{17}\text{H}_{19}]^+$ fragments, which are longer than the $[\text{C}_{15}\text{H}_{15}]^+$ fragment by one and two CH₂ groups, respectively. Despite the reduction in the range of analyzed SAMs, due to the increased length of the analyzed fragments, all the observations above are the same. Thus, the analysis performed for all three types of fragments is internally consistent and fully confirms the model formulated above.

5. CONCLUSIONS

In conclusion, a systematic analysis of static SIMS (S-SIMS) data and selected exchange experiments performed for four homologous series of SAMs, which had a general form of BPnS(Se)/Ag(Au) with $n = 2$ –6, resulted in a few interesting observations concerning the subtle changes in the internal

energetics at the metal-molecule interface induced by the substitution of the headgroup atom ($S \rightarrow Se$), and independently, the substrate ($Ag \rightarrow Au$). These observations provide a new insight, which can be divided into three important categories.

The first and most relevant insight of the current paper is the purposeful design of SAMs. These results demonstrate that the modification of the headgroup atom from S to Se increases the strength of the chemical bonding with Au and Ag, which are the most commonly used metal substrates for the formation of SAMs. It is demonstrated that the Ag substrate enables a stronger binding with both S and Se head groups in SAMs compared to Au. In addition, the obtained data indicate the influence of the structural odd–even effect on the strength of the molecule–metal binding, which is apparently weaker than the impact of the $S \rightarrow Se$ or $Au \rightarrow Ag$ substitution. Finally, it is shown that an increased strength of the chemical bonding with the metal substrate has a strong impact on the stability of consecutive chemical bonds and, in particular, leads to a reduced strength of the bond between the headgroup and the rest of the molecule. In our opinion, this effect explains the lower thermal stability of selenium-based SAMs on gold compared to sulfur analogues, as reported in previous experiments.⁵⁰ Despite the stronger bonding with the substrate for the Se-based SAMs, the thermal stability does not depend on the strongest bond but on the weakest bond in the adsorbed system; therefore, the reduced strength of the C–Se bond compared to the C–S bond may determine the lower thermal stability of Se-based SAMs. The alternative strength of the $Au(Ag)–S(Se)$ and $S(Se)–C$ bonds can also influence the conductivity of their respective SAMs. Specifically, a similar efficiency of charge transfer through the $Au–S–C$ and $Au–Se–C$ interface in SAMs was recently reported by us, which indicates that compensating the higher stability of the $Au–Se$ bond by the lower stability of the $Se–C$ bond results in an effectively similar redistribution of the electron density through the molecular framework and thus, a similar efficiency in charge transfer via the tunneling process.⁴⁷ Because our current data show that substrate modification from $Au \rightarrow Ag$ and headgroup atom modification from $S \rightarrow Se$ qualitatively have very similar effects, we may expect a similar conductance for S- and Se-based SAMs on both $Au(111)$ and $Ag(111)$ substrates. Such a conclusion is supported by recent experiments that demonstrate a very similar conductance of alkanethiols on Au and Ag substrates.⁵⁸

The second insight provided by this paper is the application of S-SIMS. In our opinion, the results conducted for very broad and systematically modified groups of SAMs constitute a new and unique application of this method. Despite using high-energy projectiles, our results show oscillations in emission of different fragments, which are related to subtle changes in the stability of internal molecular bonds of the monolayer. Such information has not been obtained so far by any other technique. Two main advantages of S-SIMS, which seem to be crucial in this study, are the following: (i) the local nature of probing, i.e., the effectively analyzed mass spectra results from the impact of a single ion with no global change to the energetic state of the sample, as is the case with more traditionally used thermal or electrochemical desorption processes, and even more importantly, (ii) the extremely short probing time, i.e., the ion-induced desorption processes occur in the picosecond time scale, in contrast to thermal or electrochemical desorption where slow ramping of the global

energies (temperature or potential energy, respectively) induces a structural evolution of the SAM/substrate system before the desorption process occurs and thus leads to a disconnected relationship between the original structure of the SAM and its stability.

The final category, and the most general one, is related to the observed oscillations in the stability of consecutive chemical bonds. This effect was identified for the first time in our recent paper,⁴⁶ which indicated that its origin is very general in chemistry and is related to breaking of the translational symmetry in molecules. Experimentally, this fundamental conclusion was based on the similar odd–even efficiency in the emission of different molecular fragments from the $BPnS(Se)/Au(111)$ series, as shown in Figure 6. For such an interpretation, however, it is necessary to prove that this effect is not related to the odd–even modification of the $BPnS(Se)/Au(111)$ SAMs structure, but it instead reflects oscillations in the internal energetics of consecutive chemical bonds in the molecules, which become visible as the n parameter of the monolayer changes due to specific experimental conditions. The direct proof presented here shows that the nature of this odd–even effect on emission is completely independent of the $Au \rightarrow Ag$ substrate modification, which leads to a reversed phase of the structural odd–even effect. Moreover, by showing the correlation between the increased binding strength upon changing the substrate ($Au \rightarrow Ag$) and the increased amplitude of these oscillations for both S- and Se-based SAMs, this paper fully confirms and expands on the earlier model proposed.

AUTHOR INFORMATION

Corresponding Author

*E-mail: piotr.cyganik@uj.edu.pl (P.C.).

ORCID

Piotr Cyganik: 0000-0001-6131-4618

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Science Centre, Poland (Grant 2011/01/B/ST4/00665). The S-SIMS equipment was purchased with the assistance of the European Regional Development Fund (Grant POIG.02.02.00-12-023/08).

REFERENCES

- (1) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chem. Rev.* **2005**, *105*, 1103–1170.
- (2) Smith, R. K.; Lewis, P. A.; Weiss, P. S. Patterning Self-Assembled Monolayers. *Prog. Surf. Sci.* **2004**, *75*, 1–68.
- (3) Ballav, N.; Thomas, H.; Winkler, T.; Terfort, A.; Zharnikov, M. Making Protein Patterns by Writing in a Protein-Repelling Matrix. *Angew. Chem., Int. Ed.* **2009**, *48*, 5833–5836.
- (4) Turchanin, A.; Götzhäuser, A. Carbon Nanomembranes from Self-Assembled Monolayers: Functional Surfaces without Bulk. *Prog. Surf. Sci.* **2012**, *87*, 108–162.
- (5) Olivier, O.; Meyer, F.; Raquez, J.-M.; Damman, P.; Dubois, P. Surface-Initiated Controlled Polymerization as a Convenient Method for Designing Functional Polymer Brushes: From Self-Assembled Monolayers to Patterned Surfaces. *Prog. Polym. Sci.* **2012**, *37*, 157–181.
- (6) Song, H.; Reed, M. A.; Lee, T. Single Molecule Electronic Devices. *Adv. Mater.* **2011**, *23*, 1583–1608.

- (7) McCreery, R. L.; Bergren, A. J. Progress with Molecular Electronic Junctions: Meeting Experimental Challenges in Design and Fabrication. *Adv. Mater.* **2009**, *21*, 4303–4322.
- (8) Kronemeijer, A. J.; Akkerman, H. B.; Kudernac, T.; van Wees, B. J.; Feringa, B. L.; Blom, P. W. M.; de Boer, B. Reversible Conductance Switching in Molecular Devices. *Adv. Mater.* **2008**, *20*, 1467–1473.
- (9) Meyerbroker, N.; Li, Z.; Eck, W.; Zharnikov, M. Biocompatible Nanomembranes Based on Pegylation of Cross-Linked Self-Assembled Monolayers. *Chem. Mater.* **2012**, *24*, 2965–2972.
- (10) Meyers, S. R.; Grinstaff, M. W. Biocompatible and Bioactive Surface Modifications for Prolonged in Vivo Efficacy. *Chem. Rev.* **2012**, *112*, 1615–1632.
- (11) Raynor, J. E.; Capadona, J. R.; Collard, D. M.; et al. Polymer Brushes and Self-Assembled Monolayers: Versatile Platforms to Control Cell Adhesion to Biomaterials. *Biointerphases* **2009**, *4*, FA3–FA16.
- (12) Cyriac, J.; Pradeep, T.; Kang, H.; Souda, R.; Cooks, R. G. Low-Energy Ionic Collisions at Molecular Solids. *Chem. Rev.* **2012**, *112*, 5356–5411.
- (13) Senoner, M.; Unger, W. E. S. Sims Imaging of the Nanoworld: Applications in Science and Technology. *J. Anal. At. Spectrom.* **2012**, *27*, 1050–1068.
- (14) Vickerman, J. C. Molecular Imaging and Depth Profiling by Mass Spectrometry—Sims, Maldi or Desi? *Analyst* **2011**, *136*, 2199–2217.
- (15) Belu, A. M.; Graham, D. J.; Castner, D. G. Time-of-Flight Secondary Ion Mass Spectrometry: Techniques and Applications for the Characterization of Biomaterial Surfaces. *Biomaterials* **2003**, *24*, 3635–3653.
- (16) Pacholski, M. L.; Winograd, N. Imaging with Mass Spectrometry. *Chem. Rev.* **1999**, *99*, 2977–3005.
- (17) Benninghoven, A. Chemical Analysis of Inorganic and Organic Surfaces and Thin-Films by Static Time-of-Flight Secondary-Ion Mass Spectrometry (ToF-Sims). *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1023–1043.
- (18) Cooper, E.; Leggett, G. Static Secondary Ion Mass Spectrometry Studies of Self-Assembled Monolayers: Influence of Adsorbate Chain Length and Terminal Functional Group on Rates of Photooxidation of Alkanethiols on Gold. *Langmuir* **1998**, *14*, 4795–4801.
- (19) Tarlov, M. J.; Newman, J. G. Static Secondary Ion Mass Spectrometry of Self-Assembled Alkanethiol Monolayers on Gold. *Langmuir* **1992**, *8*, 1398–1405.
- (20) Rading, D.; Kersting, R.; Benninghoven, A. Secondary Ion Emission from Molecular Overlayers: Thiols on Gold. *J. Vac. Sci. Technol., A* **2000**, *18*, 312–319.
- (21) Arezki, B.; Delcorte, A.; Chami, A. C.; Garrison, B. J.; Bertrand, P. Gold-Thiolate Cluster Emission from Sams under Kev Ion Bombardment: Experiments and Molecular Dynamics Simulations. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2003**, *212*, 369–375.
- (22) Arezki, B.; Delcorte, A.; Bertrand, P. Emission Processes of Molecule–Metal Cluster Ions from Self-Assembled Monolayers of Octanethiols on Gold and Silver. *Appl. Surf. Sci.* **2004**, *231*–232, 122–126.
- (23) Arezki, B.; Delcorte, A.; Garrison, B. J.; Bertrand, P. Understanding Gold-Thiolate Cluster Emission from Self-Assembled Monolayers Upon Kiloelectronvolt Ion Bombardment. *J. Phys. Chem. B* **2006**, *110*, 6832–6840.
- (24) Delcorte, A. Organic Surfaces Excited by Low-Energy Ions: Atomic Collisions, Molecular Desorption and Buckminsterfullerenes. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3395–3406.
- (25) Wong, S. C. C.; Lockyer, N. P.; Vickerman, J. C. Mechanisms of Secondary Ion Emission from Self-Assembled Monolayers and Multilayers. *Surf. Interface Anal.* **2005**, *37*, 721–730.
- (26) Nie, H. Y. Revealing Different Bonding Modes of Self-Assembled Octadecylphosphonic Acid Monolayers on Oxides by Time-of-Flight Secondary Ion Mass Spectrometry: Silicon Vs Aluminum. *Anal. Chem.* **2010**, *82*, 3371–3376.
- (27) Zhou, C.; Jones, J. C.; Trionfi, A.; Hsu, J. W. P.; Walker, A. Electron Beam-Induced Damage of Alkanethiolate Self-Assembled Monolayers Adsorbed on Gaas (001): A Static Sims Investigation. *J. Phys. Chem. C* **2010**, *114*, 5400–5409.
- (28) Arezki, B.; Delcorte, A.; Bertrand, P. Kinetic Energy Distributions of Molecular and Cluster Ions Sputtered from Self-Assembled Monolayers of Octanethiol on Gold. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2002**, *193*, 755–761.
- (29) Zharnikov, M.; Frey, S.; Rong, H.-T.; Yang, Y.-J.; Heister, K.; Buck, M.; Grunze, M. The Effect of the Sulfur-Metal Bond on the Structure of Self-Assembled Monolayers. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3359–3362.
- (30) Heister, K.; Rong, H. T.; Buck, M.; Zharnikov, M.; Grunze, M.; Johansson, L. S. O. Odd-Even Effects at the S-Metal Interface and in the Aromatic Matrix of Biphenyl-Substituted Alkanethiol Self-Assembled Monolayers. *J. Phys. Chem. B* **2001**, *105*, 6888–6894.
- (31) Rong, H. T.; Frey, S.; Yang, Y. J.; Zharnikov, M.; Buck, M.; Wühn, M.; Wöll, C.; Helmchen, G. On the Importance of the Headgroup Substrate Bond in Thiol Monolayers: A Study of Biphenyl-Based Thiols on Gold and Silver. *Langmuir* **2001**, *17*, 1582–1593.
- (32) Shaporenko, A.; Müller, J.; Weidner, T.; Terfort, A.; Zharnikov, M. Balance of Structure-Building Forces in Selenium-Based Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2007**, *129*, 2232–2233.
- (33) Weidner, T.; Shaporenko, A.; Müller, J.; Schmid, T.; Cyganik, P.; Terfort, A.; Zharnikov, M. The Effect of the Bending Potential on Molecular Arrangement in Alkaneselenolate Self-Assembled Monolayers. *J. Phys. Chem. C* **2008**, *112*, 12495–12506.
- (34) Azzam, W.; Cyganik, P.; Witte, G.; Buck, M.; Wöll, C. Pronounced Odd-Even Changes in the Molecular Arrangement and Packing Density of Biphenyl-Substituted Alkanethiol Sams. *Langmuir* **2003**, *19*, 8262–8270.
- (35) Cyganik, P.; Buck, M.; Azzam, W.; Wöll, C. Self-Assembled Monolayers of W-Biphenyl-Alkane Thiols on Au(111): Influence of Spacer Chain on Molecular Packing. *J. Phys. Chem. B* **2004**, *108*, 4989–4969.
- (36) Cyganik, P.; Szelagowska-Kunstman, K.; Terfort, A.; Zharnikov, M. Odd-Even Effect in Molecular Packing of Biphenyl-Substituted Alkaneselenol Self-Assembled Monolayers on Au(111): Scanning Tunneling Microscopy Study. *J. Phys. Chem. C* **2008**, *112*, 15466–15473.
- (37) Long, Y. T.; Rong, H. T.; Buck, M.; Grunze, M. Odd-Even Effects in the Cyclic Voltammetry of Self-Assembled Monolayers of Biphenyl Based Thiols. *J. Electroanal. Chem.* **2002**, *524*–525, 62–67.
- (38) Thom, I.; Buck, M. Electrochemical Stability of Self-Assembled Monolayers of Biphenyl Based Thiols Studied by Cyclic Voltammetry and Second Harmonic Generation. *Surf. Sci.* **2005**, *581*, 33–46.
- (39) Vervaecke, F.; Wyczawska, S.; Cyganik, P.; Bastiaansen, J.; Postawa, Z.; Silverans, R. E.; Vandeweert, E.; Lievens, P. Odd-Even Effects in Ion-Beam-Induced Desorption of Biphenyl-Substituted Alkanethiol Self-Assembled Monolayers. *ChemPhysChem* **2011**, *12*, 140–144.
- (40) Felgenhauer, T.; Rong, H. T.; Buck, M. Electrochemical and Exchange Studies of Self-Assembled Monolayers of Biphenyl Based Thiols on Gold. *J. Electroanal. Chem.* **2003**, *550*–551, 309–319.
- (41) Szelagowska-Kunstman, K.; Cyganik, P.; Schüpbach, B.; Terfort, A. Relative Stability of Thiol and Selenol Based Sams on Au(111) - Exchange Experiments. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4400–4406.
- (42) Frey, S.; Rong, H. T.; Heister, K.; Yang, Y. J.; Buck, M.; Zharnikov, M. Response of Biphenyl-Substituted Alkanethiol Self-Assembled Monolayers to Electron Irradiation: Damage Suppression and Odd-Even Effects. *Langmuir* **2002**, *18*, 3142–3150.
- (43) Cyganik, P.; Buck, M. Polymorphism in Biphenyl-Based Self-Assembled Monolayers of Thiols. *J. Am. Chem. Soc.* **2004**, *126*, 5960–5961.
- (44) Cyganik, P.; Buck, M.; Strunskus, T.; Shaporenko, A.; Wilton-Ely, J. D. E. T.; Zharnikov, M.; Wöll, C. Competition as a Design Concept: Polymorphism in Self-Assembled Monolayers of Biphenyl-Based Thiols. *J. Am. Chem. Soc.* **2006**, *128*, 13868–13878.
- (45) Cyganik, P.; Buck, M.; Strunskus, T.; Shaporenko, A.; Witte, G.; Zharnikov, M.; Wöll, C. Influence of Molecular Structure on Phase

Transitions: A Study of Self-Assembled Monolayers of 2-(Aryl)-Ethane Thiols. *J. Phys. Chem. C* **2007**, *111*, 16909–16919.

(46) Ossowski, J.; Rysz, J.; Krawiec, M.; Maciazek, D.; Postawa, Z.; Terfort, A.; Cyganik, P. Oscillations in the Stability of Consecutive Chemical Bonds Revealed by Ion-Induced Desorption. *Angew. Chem., Int. Ed.* **2015**, *54*, 1336–1340.

(47) Ossowski, J.; Wächter, T.; Silies, L.; Kind, M.; Noworolska, A.; Blobner, F.; Gnatek, D.; Rysz, J.; Bolte, M.; Feulner, P.; Terfort, A.; Cyganik, P.; Zharnikov, M. Thiolate Versus Selenolate: Structure, Stability and Charge Transfer Properties. *ACS Nano* **2015**, *9*, 4508–4526.

(48) Müller, J.; Terfort, A. Synthesis of Pure Aromatic, Aliphatic, and Araliphatic Diselenides. *Inorg. Chim. Acta* **2006**, *359*, 4821–4827.

(49) Cyganik, P.; Vandeweert, E.; Postawa, Z.; Bastiaansen, J.; Vervaecke, F.; Lievens, P.; Silverans, R. E.; Winograd, N. Modification and Stability of Aromatic Self-Assembled Monolayers Upon Irradiation with Energetic Particles. *J. Phys. Chem. B* **2005**, *109*, 5085–5094.

(50) Han, S. W.; Lee, S. J.; Kim, K. Self-Assembled Monolayers of Aromatic Thiol and Selenol on Silver: Comparative Study of Adsorptivity and Stability. *Langmuir* **2001**, *17*, 6981–6987.

(51) Riederer, D. E.; Chatterjee, R.; Rosencrance, S. W.; Postawa, Z.; Dunbar, T. D.; Allara, D. L.; Winograd, N. Thermal Desorption Induced by Kilolectronvolt Ion Bombardment of Thiol-Bound Self-Assembled Monolayers on Gold. *J. Am. Chem. Soc.* **1997**, *119*, 8089–8094.

(52) Vervaecke, F.; Wyczawska, S.; Cyganik, P.; Postawa, Z.; Buck, M.; Silverans, R. E.; Lievens, P.; Vandeweert, E. Phase-Dependent Desorption from Biphenyl-Substituted Alkanethiol Self-Assembled Monolayers Induced by Ion Irradiation. *J. Phys. Chem. C* **2008**, *112*, 2248–2251.

(53) Wyczawska, S.; Cyganik, P.; Terfort, A.; Lievens, P. Ion-Beam-Induced Desorption as a Method for Probing the Stability of the Molecule-Substrate Interface in Self-Assembled Monolayers. *ChemPhysChem* **2011**, *12*, 2554–2557.

(54) Häkkinen, H. The Gold–Sulfur Interface at the Nanoscale. *Nat. Chem.* **2012**, *4*, 443–455.

(55) Otaño, D.; Veening, T.; Brocks, G. Self-Assembled Monolayer Induced Au(111) and Ag(111) Reconstructions: Work Functions and Interface Dipole Formation. *J. Phys. Chem. C* **2012**, *116*, 7826–7837.

(56) Abufager, P. N.; Solano Canchaya, J. G.; Wang, Y.; Alcamí, M.; Martín, F.; Álvarez Soria, L.; Martiarena, M. L.; Reuter, K.; Busnengo, H. F. Theoretical Study of the Structure of Self-Assembled Monolayers of Short Alkylthiolates on Au(111) and Ag(111): The Role of Induced Substrate Reconstruction and Chain–Chain Interactions. *Phys. Chem. Chem. Phys.* **2011**, *13*, 9353–9362.

(57) Cometto, F. P.; Paredes-Olivera, P.; Macagno, V. A.; Patrito, E. M. Density Functional Theory Study of the Adsorption of Alkanethiols on Cu(111), Ag(111), and Au(111) in the Low and High Coverage Regimes. *J. Phys. Chem. B* **2005**, *109*, 21737–21748.

(58) Baghbanzadeh, M.; Simeone, F. C.; Bowers, C. M.; Liao, K. C.; Thuo, M.; Baghbanzadeh, M.; Miller, M. S.; Carmichael, T. B.; Whitesides, G. M. Odd–Even Effects in Charge Transport across N-Alkanethiolate Based Sams. *J. Am. Chem. Soc.* **2014**, *136*, 16919–16925.

Relative Thermal Stability of Thiolate- and Selenolate-Bonded Aromatic Monolayers on the Au(111) Substrate

Jakub Ossowski,[†] Giulia Nascimbeni,[‡] Tomasz Żaba,[†] Elisabeth Verwüster,[‡] Jakub Rysz,[†] Andreas Terfort,[§] Michael Zharnikov,^{||} Egbert Zojer,^{*,‡} and Piotr Cyganik^{*,†,||}

[†]Smoluchowski Institute of Physics, Jagiellonian University, Łojasiewicza 11, 30-348 Kraków, Poland

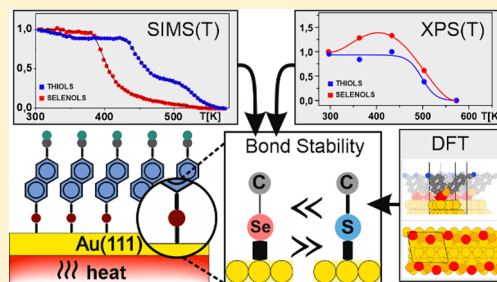
[‡]Institute of Solid State Physics, NAMI Graz, Graz University of Technology, Petergasse 16, 8010 Graz, Austria

[§]Institute of Inorganic and Analytical Chemistry, Goethe University, Max-von-Laue Str. 7, 60438 Frankfurt, Germany

^{||}Applied Physical Chemistry, Heidelberg University, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

S Supporting Information

ABSTRACT: The thermal stability of self-assembled monolayers (SAMs) is of fundamental importance for the majority of their applications. It strongly depends on the type of chemical group used for bonding the molecules forming the SAMs to the selected substrate. Here, we compare the impact of using S and Se bonding groups on the thermal stability of aromatic model SAMs based on naphthalene, containing a polar substituent, and formed on a Au(111) substrate. Using a combination of secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) while heating the samples, we show that the thermal stability of S-bonded SAMs is higher although the bonding between Se and the Au substrate is stronger. This seeming contradiction is found to result from a higher stability of the S–C compared to the Se–C bond. The latter forms the weakest link in the SAMs with Se anchor and, thus, controls its thermal stability. These conclusions are supported by state-of-the-art dispersion-corrected density functional theory (DFT) calculations. Notably, full qualitative agreement between the experiments and simulations is obtained only when including Au adatoms in the setup of the unit cells, as these reinforce the bonding between the docking groups and the metal surface. This is an indication for the occurrence of such surface reconstructions also for SAMs consisting of comparably large aromatic molecules.



I. INTRODUCTION

Self-assembled monolayers (SAMs)^{1–3} are considered as prototypical systems for investigating physical and chemical properties of organic nanostructures and their potential application in nanotechnology.^{4,5} The key to SAMs functionality is the comparably strong chemical bonding between the SAM-forming molecules and the respective substrate on which the monolayer is formed. So far, the overwhelming majority of studies analyzing fundamental properties and applications of SAMs have been conducted on molecules containing sulfur as head groups covalently bonded to the Au(111) substrates.^{3,6} In recent years it has, however, been demonstrated that selenium, which has the same valence electron configurations as sulfur, is a promising alternative for docking molecules to noble-metal substrates.⁷

One of the advantages of selenium-based SAMs on Au(111) is their better structural quality. Scanning tunneling microscopy (STM) studies of purely aromatic^{8–10} as well as hybrid aromatic–aliphatic^{11,12} selenolate SAMs on Au(111) demonstrated the formation of layers, which were superior to their thiolate analogues in terms of structural perfection, domain size, and long-range order. It has been proposed that the main reason which limits structural quality of SAMs with aromatic backbones is the stress originating from the misfit between the

structure favored by the aromatic backbones and the template provided by the Au(111) substrate.¹³ The release of this stress leads to the formation of defects and limits the achievable domain size. One of the ways to circumvent this problem is the application of hybrid aromatic–aliphatic molecules, where insertion of flexible aliphatic chains between docking group and aromatic backbone provides pathways to reduce stress without breaking the structure preferred by the aromatic moieties.¹³ This approach, however, also affects other properties of the films; it, for example, results in a significant reduction in the conductance of the monolayer. Thus, solving the stress problem via the application of another headgroup atom, i.e., selenium instead of sulfur, with no further modification of the molecular backbone is an attractive alternative solution for improving film quality, especially as this substitution does not change the conductance of the monolayer.¹⁴

The substitution of the headgroup also affects the stability of the molecule–metal bond, which is fundamental for most applications of SAMs. Despite several studies addressing the relative strength of S–Au and Se–Au bonds in SAMs, this issue

Received: September 29, 2017

Revised: November 23, 2017

Published: November 24, 2017

is still not fully clarified. Several conceptually different experimental approaches were used for the analysis including thermal desorption,^{9,15} electrochemical desorption,^{15,16} ion-induced desorption,^{14,17–19} competitive adsorption,²⁰ X-ray photoelectron spectroscopy (XPS),^{21,22} and exchange reactions.^{14,23,24} With one exception²⁴ all these experiments geared at determining stability were done by comparing SAMs with molecular backbones based on benzene,^{7,13,15,19} such as BS(Se), (C₆H₄–S(Se)), biphenyl and its derivatives^{9,16,20,21} (such as BPnS(Se), CH₃–(C₆H₄)₂–(CH₂)_n–S(Se), *n* = 2–6), or recently naphthalene¹⁴ (NC–NapS(Se), NC–C₁₀H₆–S(Se)). The majority of these reports indicates a higher stability of the Se–Au bond^{14,16–18,20,22–24} with, however, two publications^{9,21} claiming a higher stability of the S–Au bond. Interestingly, experiments arriving at contradicting conclusions (i.e., a higher stability of either S–Au^{9,21} or Se–Au^{15,16,20}) were exclusively performed on benzene-based systems comparing benzenethiol (BS) and benzeneselenol (BSe) SAMs.

In this context it is important to consider that for a meaningful comparison of the relative molecule–substrate bonding strength the studied SAMs not only need to have the same molecular backbones but they also should represent well-defined films with very similar molecular packing. Only under such conditions the impact of differences in intermolecular interactions can be minimized, and the bonding of the headgroup to the substrate becomes the main factor determining film stability. Notably, for the BS/Au(111) and BSe/Au(111), STM analysis⁹ indicates the formation of structures with packing densities differing by as much as ~40%. Moreover, high-resolution XPS (HRXPS) analysis¹⁵ reveals coadsorption of the headgroup atoms (S or Se) and unbound molecules in these SAMs. Therefore, in our opinion, a precise comparison of the stability of S–Au and Se–Au bonds using the BS/Au(111) and BSe/Au(111) SAMs is not reliable. Similar considerations apply also to investigations of the thermal stability of these SAMs, where again contradicting results have been obtained, suggesting either a lower⁹ or higher¹⁵ thermal stability of BSe/Au(111) compared to BS/Au(111).

Considering that the thermal stability of SAMs is one of the most important factors determining their range of applications, a systematic investigation of this property for SAMs differing only in the used docking atom, but otherwise having similar structures and packing densities (where the latter ought to be sufficiently high), is in high demand. Accordingly, we provide a detailed analysis of the thermal stability of the NC–NapS/Au(111) and NC–NapSe/Au(111) (see Figure 1 for chemical structures). They serve as well-defined model systems with no coadsorption of docking group atoms or unbound molecules

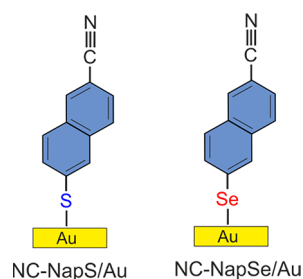


Figure 1. Schematic structures of the SAMs used in this study along with their acronyms.

seen in HRXPS.¹⁴ Moreover, they form well-ordered high-density structures displaying similar packing densities as found by STM.¹⁴

Our experimental studies rely on X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) performed on samples during heating cycles. They are supported by dispersion-corrected density functional theory (DFT) calculations, describing the stability of chemical bonds close to the metal–molecule interface for different bonding scenarios (i.e., flat Au(111) surfaces and surfaces in the presence of a varying number of adatoms). We find that a larger bonding energy between the metal and the docking group does not necessarily yield higher thermal stability. Moreover, full qualitative agreement between the experiments and calculations is achieved only when considering surface reconstructions for both SAMs.

II. EXPERIMENTAL SECTION

SAM Preparation. The Au(111) substrates were prepared by evaporating 150 nm of gold onto single crystal silicon (100) wafer substrates (ITME, Warsaw) primed with a 5 nm chromium adhesion layer (base pressure of $\sim 10^{-7}$ mbar, rate 0.5 nm/s). The synthesis of the NC–NapS(Se) molecules is described in ref 14. Following a previously developed procedure,¹⁴ SAMs were prepared by immersion of the Au(111) substrates into 1 mM solutions of the respective precursors in pure ethanol at 60 °C for 24 h. After immersion, samples were rinsed with pure ethanol, blown dry with nitrogen, and immediately transferred to the experimental setups (XPS or S-SIMS).

XPS. XPS measurements were performed with a dedicated spectrometer equipped with a hemispherical energy analyzer (VG SCIENTA R3000). The spectra were taken using a monochromatized Al K α source (*E* = 1486.6 eV; MX-650 VG Scienta). The base pressure in the analytical chamber was 5×10^{-9} mbar. The acquisition of all spectra was carried out in normal emission geometry with an energy resolution of 1.15 eV. The binding energy (BE) scale was referenced to the Au 4f_{7/2} peak at 84.0 eV. To monitor the thermal stability, the sample temperature was linearly ramped at a rate of 5 K/min. Upon reaching the desired temperature, the system was left to stabilize for 5 min, and then the measurement of the chosen signal was carried out. Because of the poor signal-to-noise ratio and the resulting long acquisition time, S and Se core-level spectra were collected in independent experiments. All spectra were fitted by symmetric Voigt functions, and a Shirley-type background was subtracted. For fitting S 2p_{3/2,1/2} and Se 3p_{3/2,1/2} doublets, two peaks with the same fwhm, a fixed branching ratio (2:1), and defined spin–orbit splitting (~ 1.2 eV²⁵ and ~ 5.40 eV,²⁶ respectively), verified by fits, were used.

S-SIMS. The SIMS experiments were performed using a time-of-flight SIMS (TOF SIMS V system, ION TOF GmbH, Germany). The instrument was operated at a base pressure of 6×10^{-10} mbar. The primary 30 keV Bi⁺ ion beam was scanned over a 500 $\mu\text{m} \times 500 \mu\text{m}$ area (128 $\times$ 128 data points) during data acquisition. The secondary ions were extracted into a reflectron TOF mass spectrometer before reaching a multi-channel plate (MCP) detector. For the thermal stability analysis, the sample temperature was linearly ramped from room temperature up to 725 K at a rate (β) of 3.75 K/min. The SIMS measurements were performed at selected temperatures without interrupting the sample heating. As discussed in the Supporting Information (Figure S1), SIMS experiments were

also performed at room temperature to prove the absence of ion-beam-induced damage of the investigated samples. These experiments confirmed the prevalence of static conditions during the SIMS measurements (S-SIMS). Before analysis, all spectra were normalized to the respective total counts.

Simulations. To analyze the bonding between the adsorbates and substrate, we calculated the energies associated with breaking S(Se)/Au and S(Se)/C bonds for a variety of adsorbate configurations using dispersion-corrected DFT. All calculations were performed using the FHI-aims code,²⁷ employing the PBE functional.²⁸ To include long-range van der Waals interactions, the latter was augmented by the Tkatchenko–Scheffler^{29,30} scheme parametrized specifically to treat adsorption on metallic surfaces (PBE+vdWsurf).³¹ The dispersion corrections between the substrate Au atoms were turned off. To model bonded monolayers on substrates and clean metal surfaces, periodic boundary conditions and the repeated slab approach were employed representing the substrate by five layers of Au. Periodic replicas of the slab were decoupled by an at least 20 Å wide vacuum gap and a self-consistently determined dipole layer to account for the electrostatic asymmetry.³² The bottom three Au layers were kept fixed in the geometry optimizations to avoid spurious relaxations at the bottom surface of the slab. As the observed energy differences between SAMs bonded by S and Se atoms in many cases are very small, it has been crucial to carefully converge the k-point sampling, the basis set (avoiding artifacts due to basis-set superposition errors), and other numerical parameters with more details given in the [Supporting Information](#). In short, Au atoms were described using the default FHI-aims “tight” settings, while for all the other atoms the default tight settings were augmented by adding a further basis function and tightening numerical settings (for more details see the [Supporting Information](#)). $6 \times 3 \times 1$, $9 \times 5 \times 1$, and $4 \times 4 \times 1$ Monkhorst–Pack k-point grids³³ were used for the rectangular ($4 \times \sqrt{3}$), rectangular ($3 \times \sqrt{3}$), and oblique ($3 \times \sqrt{7}$) unit cell, respectively. The convergence criterion for the total energy in the self-consistency cycle was set to 10^{-6} eV, and the optimizations were performed until the maximum residual force component per atom was below 0.01 eV/Å.

The primarily analyzed quantities derived from the simulations are the bonding energies (bond-breaking energies) between the docking atoms S or Se (X) and the Au surface or the first C atom (Y), E_{X-Y} . They are defined as the differences in total energy between the isolated molecular fragments, $E_{\text{mol-fragment},X-Y}$, plus the energy of the Au(111) surface (in some cases containing adatoms and/or adsorbed S/Se atoms), $E_{\text{surf},X-Y}$, and the energy of the adsorbed SAM on the Au substrate (i.e., the undisturbed, bonded SAM), $E_{\text{SAM-bonded}}$:

$$E_{X-Y} = E_{\text{mol-fragment},X-Y} + (E_{\text{surf},X-Y} - E_{\text{SAM-bonded}})/2$$

The factor of 1/2 accounts for the two molecules in the unit cell (vide infra) such that average energies per molecule are obtained. $E_{\text{surf},X-Y}$ and $E_{\text{SAM-bonded}}$ ($E_{\text{mol-fragment},X-Y}$) have been obtained using periodic (open) boundary conditions. Note that for calculating those energies, the geometries of all subsystems were fully relaxed. To assess the impact of vibrational degrees of freedom, we also calculated the vibrational eigenmodes of the bonded layer and of the individual fragments after bond-breaking for the unreconstructed rectangular ($4 \times \sqrt{3}$) unit cell employing finite displacements (for details see the [Supporting Information](#)). These calculations allowed an assessment of the impact of zero-point energies and the thermal occupation of

vibrational modes. As the vibrational energies had only a minor impact on the overall energetics and in view of the massive computational efforts associated with such calculations, we considered vibrational effects only for a single adsorption motifs, as discussed below.

III. RESULTS

Thermal Stability Analysis by XPS. To monitor the evolution of NC-NapS/Au and NC-NapSe/Au structure with temperature, signals corresponding to Au, C, S, and Se were monitored by XPS ([Figures 2–4](#)) at several different

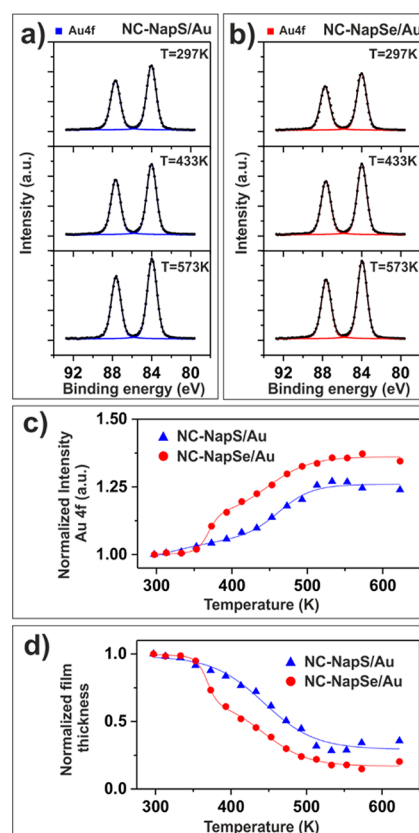


Figure 2. XPS data analysis. (a, b) Selected Au 4f spectra obtained at different temperatures for the NC-NapS/Au and NC-NapSe/Au SAMs, respectively. (c) Au 4f signal intensities normalized to the room temperature values as a function of the sample temperature measured for NC-NapS/Au (blue points) and NC-NapSe/Au (red points). (d) The normalized film thickness as a function of temperature (relative to the value at room temperature) measured for NC-NapS/Au (blue points) and NC-NapSe/Au (red points). The color-coded lines in (c) and (d) are guides to the eye.

temperatures ranging from 297 K (24 °C, room temperature) up to 623 K (350 °C). In [Figures 2a](#) and [2b](#) selected Au $4f_{7/2,5/2}$ spectra obtained for NC-NapS/Au and NC-NapSe/Au at temperatures of 297, 433, and 573 K are presented. The temperature dependence of the integrated Au $4f_{7/2,5/2}$ intensity (normalized to the room temperature value) is shown in [Figure 2c](#) for the two SAMs. It reveals a substantial difference between NC-NapS/Au and NC-NapSe/Au. Starting from 350 K (77 °C), a pronounced increase of the Au $4f_{7/2,5/2}$ signal for the NC-NapSe/Au SAM is observed, and it becomes noticeably higher than that for the NC-NapS/Au system. For the latter a somewhat steeper increase of the signal is observed only above

450 K (177 °C), but the overall signal remains lower than that for NC-NapSe/Au. Above ca. 525 K (252 °C) the signal saturates for both types of SAMs. Notably, for NC-NapSe/Au the saturation level corresponds to ca. 1.35 of the room temperature signal, while for the NapS/Au the ratio is only 1.25.

The increase of the Au 4f_{7/2,5/2} signal reflects a temperature-induced reduction in the effective SAM thickness. Assuming the standard exponential dependence of the Au 4f signal on the thickness of the adsorbate layer due to attenuation, one can determine relative changes in the effective film thickness as a function of temperature using the equation

$$\frac{d_T}{d_{T_0}} = 1 - \frac{\lambda}{d_{T_0}} \ln \left(\frac{I_{Au}(T)}{I_{Au}(T_0)} \right) \quad (1)$$

Here, d_T is the effective film thickness at elevated temperature T , d_{T_0} is the equivalent quantity at room temperature, λ is the electron mean free path, $I_{Au}(T)$ is the Au 4f intensity at temperature T , and $I_{Au}(T_0)$ is the Au 4f intensity at room temperature. Setting λ to 3.15 nm (in accordance with ref 34) and using for d_0 the values obtained in our previous HRXPS studies¹⁴ on these SAMs (1.17 nm for NC-NapSe/Au and 1.05 nm for NC-NapS/Au), the corresponding $\frac{d_T}{d_0}(T)$ values were calculated from the measured $\frac{I_{Au}(T)}{I_{Au}(T_0)}$ ratios. The resulting evolution is presented in Figure 2d. It reproduces the trend inferred from the intensity ratios, indicating a more pronounced decrease of the effective film thickness with temperature for the Se-bonded SAM.

Selected C 1s spectra for the NC-NapS/Au and NC-NapSe/Au are shown in Figures 3a and 3b, respectively, together with the temperature-dependent evolution of the peak intensities in Figure 3c. The spectra acquired at room temperature exhibit an intense peak at a BE of 284.5 eV accompanied by a shoulder at higher BE (286.0 eV). Following previous HRXPS study,¹⁴ the intense peak is assigned to the naphthalene backbone, while the high binding energy shoulder is associated with the nitrile carbon. For both types of SAMs, the integrated C 1s intensity, normalized to the value at room temperature, decreases with increasing temperature, followed by a saturation around 525 K (252 °C) (Figure 3c). This is the inverse of the behavior of the Au 4f_{7/2,5/2} signal discussed previously. Above ca. 350 K (77 °C) the normalized C 1s intensity is consistently lower for the NC-NapSe/Au layer compared to NC-NapS/Au, which is inverse to the trend observed for the Au 4f_{7/2,5/2} signal.

Interestingly, a qualitatively different behavior is observed for the S 2p_{3/2,1/2} and Se 3p_{3/2,1/2} spectra presented in Figure 4. The analysis of the integrated and normalized S 2p_{3/2,1/2} signal in Figure 4c shows a roughly constant value between room temperature and ca. 450 K (177 °C), which is followed by a drop below the detection limit of XPS for temperatures exceeding 550 K (277 °C). In contrast, for the Se 3p_{3/2,1/2} signal, an increase by ca. 25% is observed up to a temperature of ca. 400 K (127 °C), which is again followed by a sharp drop at higher temperatures.

Thermal Stability Analysis by S-SIMS. SIMS is a useful, complementary technique to study the thermal stability of SAMs.³⁵ Here, we recorded the emission intensities of characteristic secondary ions associated with the SAMs as a function of the (linearly increasing) sample temperature (a heating rate of 3.75 K/min). Two types of secondary ions were

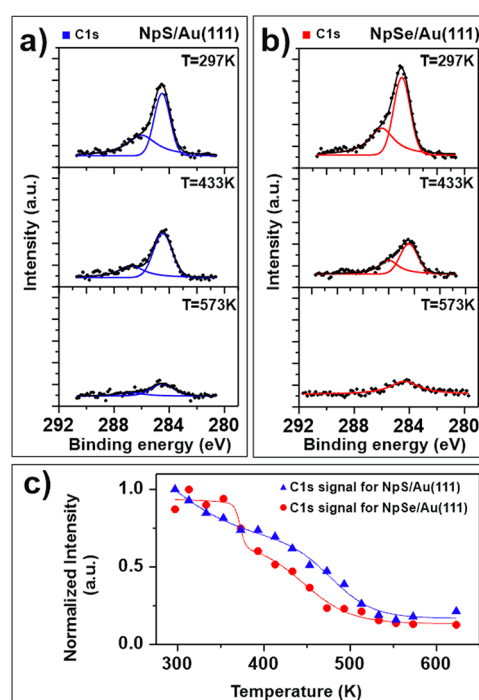


Figure 3. XPS data analysis. (a, b) Selected C 1s spectra obtained at different temperatures for NC-NapS/Au and NC-NapSe/Au, respectively (all spectra have the same vertical scale). (c) C 1s signal intensities normalized to the room temperature values as a function of the sample temperature measured for NC-NapS/Au (blue points) and NC-NapSe/Au (red points). The color-coded lines in (c) are guides to the eye.

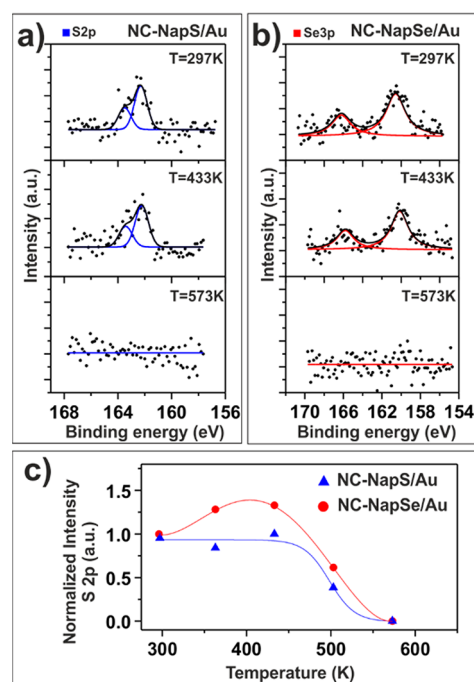


Figure 4. XPS data analysis. (a, b) Selected S 2p and Se 3p spectra obtained at different temperatures for NC-NapS/Au and NC-NapSe/Au, respectively. (c) S 2p and Se 3p signal intensities normalized to the room temperature values as a function of the sample temperature measured for NC-NapS/Au (blue points) and NC-NapSe/Au (red points), respectively. The color-coded lines in (c) are guides to the eye.

analyzed, namely “organic” ions, such as M_2Au^- (where M denotes the complete NC-NapS or NC-NapSe molecules), and “inorganic” ions, such as $AuS(Se)^-$, $AuS(Se)_2^-$, and $Au_2S(Se)^-$. To ensure that the measured intensity changes analyzed in the thermal SIMS experiments are not related to primary ion beam damage during the data acquisition, separate reference experiments monitoring the intensity of the analyzed signals at room temperature for 110 scans were conducted (see Figure S1 in the Supporting Information). These data show that during the entire measurement time needed for the thermal analysis (65 scans in Figure 5 and 95 scans in Figure 6) all signals remain constant. From this behavior one can conclude that all experiments were conducted in the static SIMS (S-SIMS) mode.

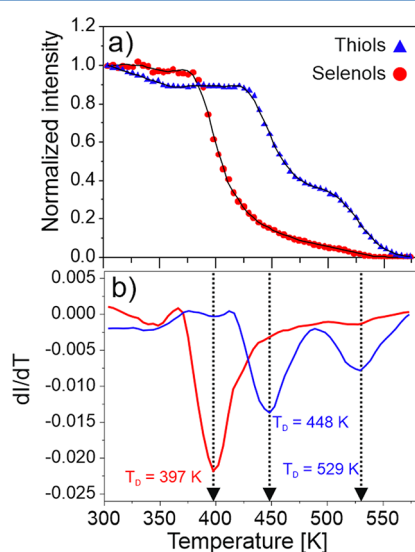


Figure 5. S-SIMS data analysis. (a) shows M_2Au^- secondary ion intensities normalized to the room temperature values as a function of the sample temperature measured for NC-NapS/Au (blue points) and NC-NapSe/Au (red points). Solid lines in (a) show the spline function fitted to the data points to enable the data processing. (b) Derivatives of the experimental curves in (a) (calculated from the aforementioned spline functions) for NC-NapS/Au (blue line) and NC-NapSe/Au (red line). The desorption temperatures (T_D) corresponding to the minima of the derivatives are indicated.

The signal for the “organic” M_2Au^- secondary ion provide information on changes in the coverage for a given SAM as a function of the temperature ramping. In fact, metal–organic secondary ions like M_2Au^- are well-known “fingerprints” for SAM formation and desorption analysis in SIMS.^{35–41} The “inorganic” secondary ion group can be used to trace the stability of the bonding between the headgroup atom and the substrate.

Figure 5a shows changes in the emission intensity of the M_2Au^- secondary ions as a function of temperature in the range between room temperature and 570 K (297 °C). To enable a direct comparison of both types of SAMs, the data presented in Figure 5a are normalized to the values measured at room temperature. For both types of SAMs, an approximately constant signal intensity is observed up to a certain temperatures, which is followed by an intensity drop to zero at the higher temperatures. The character of the signal decrease is, however, substantially different between NC-NapS/Au and NC-NapSe/Au. While for the Se-bonded SAM a single sharp

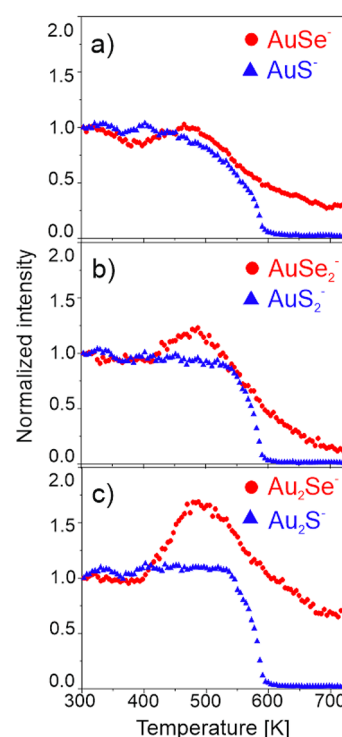


Figure 6. S-SIMS data analysis. (a) AuS^- and $AuSe^-$ secondary ion intensities normalized to the room temperature values as a function of the sample temperature measured for NC-NapS/Au (blue points) and NC-NapSe/Au (red points) SAMs. (b) Equivalent data for the AuS_2^- and $AuSe_2^-$ secondary ions, and (c) displays them for the Au_2S^- and Au_2Se^- secondary ions.

drop is observed, which starts already below 400 K (127 °C), the signal for the S-bonded SAM decreases in two steps, which both occur at significantly higher temperatures. To determine the temperatures characteristic of the observed drops of the M_2Au^- signal, the first derivative of the normalized intensity as a function of temperature was calculated (Figure 5b). This derivative yields a single characteristic temperature of 397 K (124 °C) for the NC-NapSe/Au, indicative of a single thermal desorption process. In contrast, for the NC-NapS/Au, two minima at 448 K (175 °C) and 529 K (256 °C) are obtained, indicative of two successive desorption processes which set in at significantly higher temperatures. We note here that such a two-step desorption process is not visible in the temperature-dependent XPS data (Figures 2 and 3) which are acquired with a much slower procedure (27 min per each temperature step in XPS in contrast to only 1 min in SIMS) and with much lower resolution (16 points for the whole temperature range in XPS, in contrast to 74 points in SIMS). Provided that the change in the SIMS signal intensity is proportional to the surface coverage, Θ , of the NC-NapS/Au, the first desorption process reduces the coverage by ca. 60%. Assuming first-order kinetics of all observed processes, one can estimate the value of the corresponding desorption energy E_D using the Redhead formula:⁴²

$$E_D = kT_p \left[\ln \left(\frac{\nu_T T_p}{\beta} \right) - 3.64 \right] \quad (2)$$

where k is the Boltzmann constant, T_p is the peak temperature (i.e., the temperature where the change in the surface coverage Θ is most pronounced and $d\Theta/dT$ becomes a minimum), ν_T is

the frequency factor (which is usually approximated as ca. 10^{13} s^{-1}),^{9,15,43,44} and $\beta = 3.75 \text{ K/min}$ is the heating rate. For the NC-NapSe/Au, $T_p = 397 \text{ K}$ yields a value of $E_D = 1.20 \text{ eV}$; for the NC-NapS/Au the two characteristic temperatures of $T_p = 448 \text{ K}$ (175°C) and $T_p = 529 \text{ K}$ (256°C) correspond to $E_D = 1.35 \text{ eV}$ and $E_D = 1.61 \text{ eV}$, respectively.

The analysis of the “inorganic” signals corresponding to the $\text{AuS}(\text{Se})^-$, $\text{AuS}(\text{Se})_2^-$, and $\text{Au}_2\text{S}(\text{Se})^-$ secondary ions is presented in Figure 6. All three signals exhibit significant differences for the NC-NapS/Au and NC-NapSe/Au. First, for NC-NapS/Au an abrupt drop of the signals is observed above ca. 500 K (227°C) reaching zero above ca. 600 K (327°C). In contrast, for NC-NapSe/Au an increase of the signals is observed in the region between ca. 400 K (127°C) and 450 K (177°C), which is especially pronounced for the AuSe_2^- and Au_2Se^- ions. Additionally, for NC-NapSe/Au a significant intensity of all signals is observed even at 725 K (452°C), i.e., at the upper temperature limit of our experiments.

Simulations. To further analyze the bonding between the docking groups and the substrate, as well as bonding between the docking groups and the molecular backbone, we calculated the energies associated with the breaking of these bonds for a variety of adsorbate configurations. These simulations follow the approach usually applied for computing stabilities of adsorbate layers, namely comparing the energy differences between SAMs adsorbed on the substrate and molecules detached from the surface. What they do not take into account are the details of the desorption process. Unfortunately, a meaningful simulation of the dynamics of molecular desorption for system as complex as the present ones is currently intractable by computational techniques, which provide the accuracy required for the present problem (see below). One of the reasons for that is that thermally initiated desorption most likely occurs from the rims of islands or from disordered regions of the adsorbate layer. The simulation would require the consideration of huge supercells. Therefore, we restrict the following analysis to bond-breaking energies (for further details see Experimental Section). In this context it is however, worthwhile mentioning that calculations on phenyl thioliates and selenolates at low coverage by Cometto et al.¹⁵ suggest that energy differences and activation barriers are intimately related for systems like the present one.

Notably, in the simulations considering a translational periodicity of the substrate and the adsorbate, we need to consider adsorbate unit cells that are also commensurate with the periodicity of the unreconstructed Au(111) surface. Moreover, even with state-of-the-art resources, simulations like the present ones are limited to a few hundred atoms in the unit cell. These aspects prevented us from directly adopting the large ($2\sqrt{3} \times \sqrt{37}$) unit cell identified experimentally¹⁴ for the NC-NapS/Au SAM or the ($2 \times 1.5\sqrt{3}$) adsorbate unit cell reported for the NC-NapSe/Au SAM, which is non-commensurate with the Au substrate. Consequently, we identify computationally affordable unit cells commensurate with the periodicity of the unreconstructed Au(111) surface, in which the SAMs display packing densities similar to the ones obtained in the respective experiments. Therefore, in our simulations we considered three different unit cells containing two molecules arranged in a herringbone pattern, as identified for the related anthraceneselenolates^{10,45} on the Au(111) substrate (see Figure 7). The first is the commensurate rectangular ($3 \times \sqrt{3}$) unit cell, which has the same area per molecule (0.215 nm^2) as the incommensurate rectangular ($2 \times$

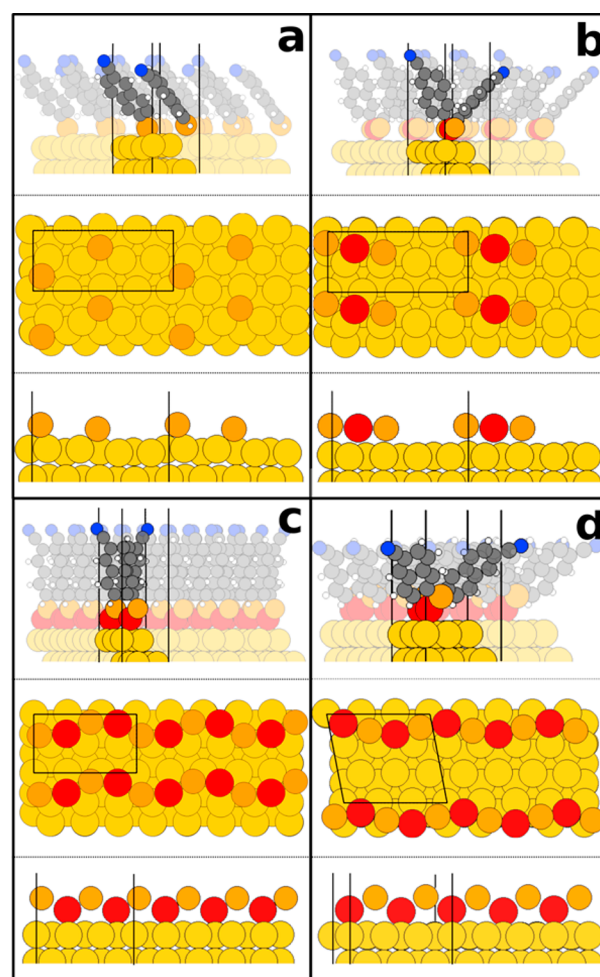


Figure 7. Top and side views of exemplary unit cells of the NC-NapS and NC-NapSe adsorbates on Au(111) after geometry optimization. All unit cells contain two molecules in herringbone arrangement, and in the bottom two panels of each plot, the molecular backbones are not displayed to more clearly show the relative positions of the gold adatoms and the docking groups. (a) Rectangular ($4 \times \sqrt{3}$) surface unit cell with unreconstructed Au surface; (b) rectangular ($4 \times \sqrt{3}$) surface unit cell containing one gold adatom; (c) rectangular ($3 \times \sqrt{3}$) surface unit cell containing two gold adatoms; (d) oblique ($3 \times \sqrt{7}$) unit cell containing two adatoms. Au atoms are yellow and adatoms red; docking atoms (S or Se) are orange, C atoms gray, H atoms white, and N atoms blue.

$1.5\sqrt{3}$) unit cell observed¹⁴ in previous STM experiments on the NC-NapSe/Au interface as the closest approximation to the real structure (bearing in mind the finite experimental resolution). The molecules in that unit cell are tightly packed with the area per molecule slightly smaller than in some of the reported naphthalene crystal structures.¹⁴ In spite of considerable efforts, this very tight packing prevented convergence of the self-consistent field cycles in the absence of reconstructions of the Au(111) surface. Therefore, we also considered a larger commensurate rectangular ($4 \times \sqrt{3}$) surface unit cell with an area per molecule of 0.287 nm^2 . Notably, the ($4 \times \sqrt{3}$) surface unit cell is also the one found for anthraceneselenolate SAMs on Au(111).¹⁰ Finally, we also tested an even larger commensurate oblique ($3 \times \sqrt{7}$) cell with an area per molecule of 0.323 nm^2 . This served to evaluate the impact that an increased molecular tilt angle, occurring at lower coverages, has on binding energies. In passing, we note that the above

Table 1. Bond-Breaking Energies (E_{S-C} , E_{Se-C} , E_{Au-S} , E_{Au-Se}) and Respective Differences ($\Delta E_{S/Se-C}$, $\Delta E_{Au-S/Se}$) for All Studied Systems Together with the Average Tilt Angles of Each Conformation and the Order of the Bonding Energies

unit cell recon	rectangular ($4 \times \sqrt{3}$)			rectangular ($3 \times \sqrt{3}$)		oblique ($3 \times \sqrt{7}$)
	none	1 ad	2 ad	1 ad	2 ad	2 ad
E_{S-C} (eV)	3.003	3.286	3.252	3.144	3.044	3.223
E_{Se-C} (eV)	2.696	2.888	2.883	2.772	2.725	2.880
$\Delta E_{S/Se-C}$ (eV)	-0.307	-0.398	-0.369	-0.372	-0.319	-0.343
E_{Au-S} (eV)	2.544	2.892	3.104	2.748	3.214	3.358
E_{Au-Se} (eV)	2.625	2.912	3.120	2.798	3.313	3.413
$\Delta E_{Au-S/Se}$ (eV)	0.081	0.020	0.016	0.050	0.099	0.055
av tilt (deg)	47	38	38	14	19	57
order	S-C > Se-C $\geq$ Au-S $\geq$ Au-Se	S-C > Au-Se $\geq$ Au-S $\geq$ Se-C	S-C > Au-Se $\geq$ Au-S $\geq$ Se-C	S-C > Au-Se $\geq$ Se-C $\geq$ Au-S	Au-Se > Au-S > S-C > Se-C	Au-Se > Au-S > S-C > Se-C

areas per unit cell are reported for the experimental Au(111) lattice constant of 0.286 nm while in the simulations the equilibrium lattice constant for the employed methodology has been used (0.294 nm) in order to avoid spurious relaxations of the surface atoms during the geometry optimizations.

In addition to varying the size of the unit cells, we also considered several adatom motifs discussed in the literature.^{6,46} This is insofar relevant in the present context, as reconstructions of the Au(111) surface are expected to modify the bonding between the docking atom (S or Se) and the substrate, which in turn also changes the bonding between S(Se) and the adjacent C atom.^{14,17,18} Moreover, the existence and nature of surface reconstructions have been intensively (and sometimes controversially) discussed for short-chained thiolates. Still, very little is known regarding comparably large conjugated backbones like the anthracenes considered here. Thus, the comparison between the calculated and measured trends discussed in the following will also provide valuable insight into the nature of surface reconstructions in such systems. In particular, we considered the following:

(i) A flat unreconstructed Au(111) surface (see Figure 7a; calculated only for the rectangular ($4 \times \sqrt{3}$) surface unit cell due to the above-described convergence problems): There we find the molecules bonded to the substrate with the S/Se atoms in the fcc-hollow sites shifted toward the bridge.

(ii) A reconstructed surface with one adatom per unit cell located on a bridge site as suggested in ref 6 (see Figure 7b; calculated for the rectangular ($3 \times \sqrt{3}$) and ($4 \times \sqrt{3}$) unit cells): There the docking atoms coordinate with the adatom and with an atom of the regular surface, which shifts them to a position between fcc-hollow and on-top.

(iii) A reconstructed surface with two adatoms per unit cell^{6,46} (see Figure 7c,d; calculated for the rectangular ($3 \times \sqrt{3}$), the rectangular ($4 \times \sqrt{3}$), and the oblique ($3 \times \sqrt{7}$) surface unit cells): For the rectangular ($3 \times \sqrt{3}$) and oblique ($3 \times \sqrt{7}$) unit cells, each docking atom is coordinated with two adatoms, the S and Se atoms are lifted from the surface, and docking atoms and adatoms form an alternating chain on the surface. Conversely, for the optimized structure in the rectangular ($4 \times \sqrt{3}$) unit cell the second adatom appears not to interact very strongly with the adjacent docking atom (see Supporting Information).

The relative stabilities of the adatom structures are discussed in detail in the Supporting Information where also structures of all calculated systems are shown.

The bond-breaking energies calculated for all considered systems are summarized in Table 1 with the energy differences between S and Se docking atoms plotted in bold. In all studied configurations, $\Delta E_{S/Se-C}$ is negative; i.e., the bonding energy between S and C is always higher than between Se and C, independent of the considered unit cell or adatom structure. Conversely, $\Delta E_{Au-S/Se}$ is always positive, indicating that the binding energy between Se and Au is consistently larger than between S and Au (albeit differences here are comparably small). These observed opposing trends for bonding between the docking atom and the substrate and the backbone support the notion that strengthening one of the bonds weakens the other.^{14,17,18}

Interestingly, the relative strength of the bonds between the docking atom and either the metal substrate or the nearest C atom strongly depends on the number of adatoms per unit cell. For an unreconstructed surface, the bonds of both S and Se to C (i.e., to the molecular backbone) are stronger than those to Au. Adding adatoms, however, reinforces the bonds between the docking atoms and the substrate. For only one adatom per unit cell, this results in nearly identical bonding energies for the Se-C and Au-S bonds. With two adatoms per unit cell the bonding strength to the substrate increases further and for the rectangular ($3 \times \sqrt{3}$) and oblique ($3 \times \sqrt{7}$) unit cells, the Au-Se becomes the strongest of the considered bonds. Concomitantly, the Se-C bond becomes the weakest (notably, for all analyzed cells with two adatoms). The particularly large bonding energies to the substrate for two adatoms in the rectangular ($3 \times \sqrt{3}$) and oblique ($3 \times \sqrt{7}$) unit cells can be tentatively attributed to the formation an alternating chain of adatoms and docking atoms lifted from the surface (see structures in Figure 7). For such a situation one obtains a bonding energy order of $E_{Au-Se} > E_{Au-S} > E_{S-C} > E_{Se-C}$. This order prevails independent of the molecular tilt angle, which in our calculations varies from 19° (in the rectangular ($3 \times \sqrt{3}$) structure) to 57° (in the oblique ($3 \times \sqrt{7}$) structure).

The biggest impact of the vibrational contributions to bond-breaking energies is expected for the Au-S/Se bonds, as then the masses of the leaving fragments differ considerably; moreover, even when the SAM is still intact, a vibration involving the Au-S(Se) bond is expected to most strongly depend on the docking atom considering the significant differences in the oscillating masses. Thus, we only tested the impact of vibrational energies on breaking the bond between the two docking atoms (S or Se) and the (unreconstructed) Au surface. Here we found only a small increase in the bonding

asymmetry between S–Au and Se–Au from 0.085 eV (when disregarding vibrations) to 0.098 eV (when including the zero-point energy) and to 0.120 eV (when considering the thermal occupation of vibrational modes at room temperature). A more detailed discussion of vibrational contributions can be found in the [Supporting Information](#).

As another possible scenario, we tested the desorption of molecules as dithiols, as this has been discussed in several publications on aliphatic thiolates.^{43,47–50} A comprehensive study of all possible leaving fragments goes beyond the scope of the present article, but it should be mentioned that the binding energy of a dithiol (i.e., the energy difference of the dithiol minus 2 times the energy of the individual radicals) is 0.080 eV larger than that of the diselenols (2.239 eV for dithiols and 2.160 for diselenols). This would make it energetically less costly to break Au–S bonds compared to Au–Se bonds provided that dimer desorption is a favorable process also for the present systems.

A final “word of warning” concerns the impact of disorder: As mentioned earlier, desorption is not to be expected from perfectly packed films, but from rims of islands and disordered portions of the films; thus, calculating surfaces with perfect lateral periodicity can only approximate the real situation. Still, it is interesting to see that aspects like molecular tilt (potentially varying significantly in disordered areas) have only a comparably minor impact on bonding strengths. In contrast, the actual structure of the substrate (i.e., the presence of adatoms) and, thus, the local bonding partners of the docking atoms are crucial for the interface energetics.

IV. DISCUSSION

The key conclusion that can be drawn from the above experiments is that the Se-bonded SAMs are thermally less stable than their thiolate counterparts. This can, for example, be inferred from the faster decrease of the nominal film thickness with heating that is observed in the XPS experiments on Se-bonded films. It is also consistent with the larger film thickness at saturation range above 525 K (252 °C) observed for S-bonded SAMs ([Figure 2](#)): The saturation of the signals at high temperatures is consistent with previous observations on biphenylthiol-based SAMs^{51,52} and can be attributed to the binding of the carbonaceous fragments to defects and steps on the gold substrate.⁵³ The saturation level is primarily determined by the amount of material still present on the surface. Therefore, the higher saturation levels for the S-bonded SAM is another aspect testifying to its increased thermal stability.

A more quantitative picture is obtained from the S-SIMS experiments (employing a much faster annealing procedure than for XPS). The temperature evolution of the M_2Au^+ signal not only confirms the higher thermal stability of the thiol-bonded monolayer but also allows extracting activation energies. For the NC-NapSe/Au desorption takes place in a single step with an estimated activation energy of $E_D = 1.20$ eV. In contrast, for the NC-NapS/Au desorption occurs in two steps. The first and major step (~60% reduction in coverage) corresponds to an activation energy of $E_D = 1.35$ eV, which is noticeably higher than the activation energy for selenolate desorption. Like the single desorption step for the NC-NapSe/Au, it is attributed to desorption of molecules from the initial high density structures of both SAMs, i.e., presumably from the rims of islands of upright-standing molecules. The second step for the NC-NapS/Au at $E_D = 1.61$ eV corresponds to

desorption from a low density (~40% of initial coverage) structure. It is tentatively associated with an adsorbate film consisting of strongly tilted molecules,⁵⁴ with the backbones interacting with the surface by van der Waals interactions (in addition to the headgroup–substrate bond).^{55,56} This leads to an overall increase of the binding energy per molecule.

The observation of a more strongly bonded phase at low coverages in NC-NapS/Au is insofar important, as it strongly supports our statement in the [Introduction](#) that for understanding the fundamental reasons for the thermal stability of molecule–metal interface one has to compare desorption from equivalent (typically high density) phases with similar structures. As this is the case for NC-NapS/Au and NC-NapSe/Au, with microscopically and spectroscopically well-characterized structure,¹⁴ this justifies an estimation of the difference in desorption energies between NC-NapS/Au and NC-NapSe/Au. It amounts to $\Delta E_D = 0.15$ eV. Notably, even for well-defined samples like the present ones, this value is associated with a non-negligible error bar, as choosing a frequency factor of 10^{16} s^{-1} Hz (as it has been done in refs 35 and 43), in contrast to the 10^{13} s^{-1} Hz used above (to be consistent with refs 9, 15, and 57), increases that difference to $\Delta E_D = 0.20$ eV.

The obtained value of $\Delta E_D = 0.15$ eV is very close to the desorption-energy difference of $\Delta E_D = 0.12$ eV, which has been derived from thermal desorption spectroscopy (TDS) data for phenylthiol (BS) and phenylselenol (BSe) SAMs on Au employing the Redhead formula with the same frequency factor of 10^{13} s^{-1} as used here.⁹ Interestingly, in those systems, a two-step desorption has been observed for both docking groups, and consistent with what has been stated above, the quoted value corresponds to desorption from the high-density phase. In contrast, recent *ex situ* studies in nitrogen atmosphere of the BS/Au and BSe/Au surface coverage changes as a function of thermal annealing¹⁵ yielded, for high density phases, a much smaller difference in desorption energies of only 0.03 eV.

What still needs to be clarified is the reason for the reduced thermal stability of the Se-docked SAMs in spite of the typically observed stronger bonding of that group to the metal surface (refs 14, 16–18, 20, 22, and 23; [Table 1](#)). This question can be addressed on the basis of the S 2p/Se 2p XPS spectra and the $AuSe(S)_2^-$ and $Au_2Se(S)^-$ S-SIMS data, where the S-SIMS experiments benefit from a much higher signal-to-noise ratio. Moreover, XPS and S-SIMS provide complementary information. The XPS signal intensities are determined by two competing trends: On the one hand, the S/Se signal drops due to the desorption of the S and Se atoms from the surface (potentially with attached molecular backbones). This process dominates, when the Se/S–Au bonds are broken. On the other hand, an increase of the S 2p/Se 2p XPS signals is possible, when the Se/S–C bond breaks and the docking atoms remain on the substrate, as then the attenuation of the photoelectron signal is reduced due to a decreased effective thickness of the hydrocarbon film. Following these arguments, the initial increase of the Se 3p signal for the NC-NapSe/Au sample in the temperature range between 350 and 450 K ([Figure 4c](#)) is a clear indication for an efficient scission of the bond between Se and the adjacent C atom of the molecular backbone. Conversely, the S 2p signal remains constant in the given temperature range. As the C 1s signal drops upon heating the sample (to about 50% at 450 K, [Figure 3c](#)), this indicates that also for the NC-NapS/Au system the S–C scission occurs

accompanied by a breaking of the S–Au bond. We note at this point that efficient breaking of the S–C bond during thermal annealing of thiols has been reported earlier for both aromatic and aliphatic SAMs formed on different metal substrates such as Au,^{51,52,58} Cu,⁵⁹ and Ni.⁶⁰ The data obtained here for NC-NapS/Au and NC-NapSe/Au systems show that temperature-induced Se–C bond scission is more effective than the S–C bond breaking.

S-SIMS provides information on the desorbing ions without being affected by signal attenuation effects. Still, the AuSe^- , AuSe_2^- , and Au_2Se^- signals increase significantly at temperature above 400 K, i.e., at a temperature corresponding to the onset of the desorption process for the NC-NapSe/Au (see Figure S5). This indicates a much higher efficiency of Se–C bond scission than for the Au–Se bond at an elevated temperature. In contrast, the AuS^- , AuS_2^- , and Au_2S^- signals remain constant, supporting the assumption of a much more balanced efficiency for S–C and Au–S bond breaking.

The above conclusions are in agreement with the results of a recent study on the same SAMs as investigated here, probing the relative stability of S–C and Se–C bonds by ion-induced desorption.¹⁴ There, as an explanation for the comparably weak bonding between the Se and the C atoms, it has been suggested that a higher involvement of the headgroup atom in the chemical bonding with the Au(111) substrate reduces its involvement in the chemical bonding to the molecular backbone.¹⁴ Ion-desorption experiments for a homologues series of biphenyl substituted aliphatic SAMs ($\text{Au}(\text{Ag})\text{--S}(\text{Se})\text{--}(\text{CH}_2)_n\text{--C}_6\text{H}_4\text{--C}_6\text{H}_4\text{--CH}_3$, $n = 2\text{--}6$) have, in fact, suggested that this effect is rather general and leads to an oscillation in stability of consecutive chemical bonds in molecular adsorbates.^{17,18}

Overall, the current thermal stability experiments in conjunction with former SIMS^{14,17,18} and exchange²³ experiments imply the following sequence of bonds stabilities: $\text{Au--Se} > \text{Au--S} > \text{C--S} > \text{C--Se}$. Notably, especially the S-SIMS data provide further insight into the interface properties. They, for example, hint toward a possible existence of adatoms: The observed increase of the signal of the “inorganic” ions is much more pronounced for AuSe_2^- and Au_2Se^- secondary ions compared to AuSe^- , which indicates that AuSe_2^- and Au_2Se^- signals more directly follow the changes in Se concentration on Au surface. Assuming that Au and Se atoms in these secondary ions reflect the original bonding geometry at the molecule–metal interface, this observation would be consistent with the adsorption model involving adatoms,^{6,38–40} in which the headgroup atom forms chemical bonds with two Au adatoms (forming Au_2Se^-) and the Au adatom binding with two headgroup atoms (forming AuSe_2^-).

Information on the fate of the docking atom can be gained from the S-SIMS data at higher temperatures: For the AuS^- , AuS_2^- , and Au_2S^- signals a sharp drop is observed down to the zero level at 600 K (327 °C), where also the signal from the molecules traced by the M_2Au^+ emission has vanished completely. This suggests a complete removal of the S atoms from the surface. The drop in the AuSe^- , AuSe_2^- , and Au_2Se^- signals is more gradual, and even at the highest tested temperature (725 K) the associated signal does not reach the zero level. This hints toward a particularly strong bonding of the Se atoms to the Au substrate preventing their complete desorption, which is fully consistent with literature reports on the formation of Au–Se alloys at temperatures above 613 K.⁶¹

Comparing the experimentally determined data to the results of the calculations, several interesting observations can be made: (i) Consistent with the current thermal experiments and former bonding stability analysis,^{14,17,18} the Se–C bond is weaker than the S–C bond for all considered unit cells and surface reconstructions. In line with the arguments from refs 14, 17, and 18 that strengthening the bond between the docking atom and one partner weakens the bond to the other partner, this results in the Se–Au bond being stronger than the S–Au one. (ii) Whether or not the links to C or to the Au atoms are the weakest elements of the SAM depends on the presence of adatoms. These strengthen the bonds to the (reconstructed) Au surface and, consequently, weaken the bonds to the C backbone. As a result, the Se–C bond represents the weakest link also in the simulations, but only when adatoms are considered (typically for two adatoms per unit cell, but in the case of a rectangular ($4 \times \sqrt{3}$) unit cell also for one). Finally, and most importantly, the sequence of bonds stability which has been deduced from the experiments, i.e., $\text{Au--Se} > \text{Au--S} > \text{C--S} > \text{C--Se}$, is observed exclusively for rectangular ($3 \times \sqrt{3}$) and oblique ($3 \times \sqrt{7}$) unit cells containing two adatoms. Note that the latter unit cell is contained here only for comparative reasons to show that the adatoms rather than details of the molecular arrangement determine the order in bond strength. Its comparably large molecular footprint (0.323 nm^2) is not compatible with experimental values for the NC-NapSe/Au (0.215 nm^2) and NC-NapS/Au (0.239 nm^2). This suggests the rectangular ($3 \times \sqrt{3}$) unit cell with two adatoms per unit cell as the most likely scenario (at least among the ones considered here), which is also supported by the observation that for that unit cell we calculate the highest SAM-formation energy per surface area (see Table S4 in the Supporting Information).

Finally, we note that the experimentally obtained difference in desorption energies for NC-NapS/Au and NC-NapSe/Au (0.15 eV) is smaller than the difference in the S–C and Se–C bond stability (0.32 eV) calculated for the rectangular ($3 \times \sqrt{3}$) unit cell with two adatoms. Besides the uncertainty of the experimental value linked to the choice of the frequency factor (see above), a possible explanation for that is that in the calculations we consider the breaking up of the continuous SAM into individual molecules and a substrate still containing the surface reconstructions, while the actual thermal desorption of molecules happens from the rim of molecular islands with modified molecule–molecule and molecule–substrate interactions. This is also almost certainly the reason for very large absolute values of the calculated bond-breaking energies. Moreover, as described in the Results section, also the nature of the actually leaving species does have some impact on the exact energetics of the process. Independent of these complications, the simulations clearly support the qualitative picture that arises from the thermal stability experiments.

V. SUMMARY AND CONCLUSIONS

Two independent sets of experiments based on the XPS and S-SIMS techniques were performed for probing the influence of the bonding group (S or Se) on the thermal stability of prototypical aromatic SAMs on the Au(111) substrate. Both types of experiments unequivocally demonstrated a higher thermal stability of thiolate-bonded SAMs with the quantitative analysis by SIMS showing ca. 0.15 eV higher desorption energy for that system.

This is insofar surprising, as most experiments suggest a lower stability of the S–Au compared to the Se–Au bond. The

apparent contradiction is resolved by showing that not Se–Au but Se–C is the actual weak link in the studied SAMs, i.e., that the lower thermal stability of the selenolate-bonded layers is a consequence of a preferential scission of the bond between the docking group and the backbone. The experimental studies are augmented by state-of-the-art DFT simulations which confirm the main trends seen experimentally. Interestingly, to fully reproduce the order of the bond strengths suggested by the experiments ($\text{Au–Se} > \text{Au–S} > \text{C–S} > \text{C–Se}$), it is necessary to include two adatoms per surface unit cell in the simulations. This hints toward the prevalence of such reconstructions not only in S-bonded but also in Se-bonded monolayers. The obtained order in the bond strengths supports the notion that a higher involvement of the bonding atom in the chemical linking to the substrate weakens its bond to the molecular backbone. From a design point of view, the present results show that for obtaining SAMs with higher thermal stability, one cannot simply follow the strategy of selecting a docking group with a particularly high bonding strength to the substrate but needs to finely balance the strength of the bonding between docking group and the substrate and between docking group and molecular backbone.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b09685.

Additional details regarding the S-SIMS analysis as well as the theoretical approach including a description of the chosen starting geometries, the optimization procedure, the simulations of vibrational properties, and the overview of calculated SAM-formation energies (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: piotr.cyganik@uj.edu.pl (P.C.).

*E-mail: egbert.zojer@tugraz.at (E.Z.).

ORCID

Andreas Terfort: 0000-0003-2369-5151

Michael Zharnikov: 0000-0002-3708-7571

Egbert Zojer: 0000-0002-6502-1721

Piotr Cyganik: 0000-0001-6131-4618

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Mr. Marek Drozdek (Department of Chemistry, Jagiellonian University) for his assistance in collecting the XPS data and O. T. Hofmann (Institute of Solid State Physics, Graz University of Technology) for stimulating discussions especially regarding the modeling data. This work was financially supported by the National Science Centre, Poland (Grant DEC-2013/10/E/ST5/00060). The S-SIMS and XPS equipment was purchased with the assistance of the European Regional Development Fund (Grant POIG.02.02.00-12-023/08). Financial support by the Austrian Science Fund (FWF), P24666-N20 and I2081-N20, is gratefully acknowledged. The computational results presented have been achieved using the Vienna Scientific Cluster (VSC). J.O. acknowledges support from START fellowship by

Foundation for Polish Science (FNP). M.Z. appreciates financial support of the German Research Foundation (DFG).

■ REFERENCES

- (1) Ulman, A. Formation and Structure of Self-Assembled Monolayers. *Chem. Rev.* **1996**, *96*, 1533–1554.
- (2) Schreiber, F. Self-Assembled Monolayers: From 'Simple' Model Systems to Biofunctionalized Interfaces. *J. Phys.: Condens. Matter* **2004**, *16*, R881–R900.
- (3) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chem. Rev.* **2005**, *105*, 1103–1170.
- (4) Casalini, S.; Bortolotti, C. A.; Leonardi, F.; Biscarini, F. Self-Assembled Monolayers in Organic Electronics. *Chem. Soc. Rev.* **2017**, *46*, 40–71.
- (5) Xiang, D.; Wang, X.; Jia, C.; Lee, T.; Guo, X. Molecular-Scale Electronics: From Concept to Function. *Chem. Rev.* **2016**, *116*, 4318–4440.
- (6) Häkkinen, H. The Gold–Sulfur Interface at the Nanoscale. *Nat. Chem.* **2012**, *4*, 443–455.
- (7) Romashov, L. V.; Ananikov, V. P. Self-Assembled Selenium Monolayers: From Nanotechnology to Materials Science and Adaptive Catalysis. *Chem. - Eur. J.* **2013**, *19*, 17640–17660.
- (8) Shaporenko, A.; Cyganik, P.; Buck, M.; Ulman, A.; Zharnikov, M. Self-Assembled Monolayers of Semifluorinated Alkaneselenolates on Noble Metal Substrates. *Langmuir* **2005**, *21*, 8204–8213.
- (9) Käfer, D.; Bashir, A.; Witte, G. Interplay of Anchoring and Ordering in Aromatic Self-Assembled Monolayers. *J. Phys. Chem. C* **2007**, *111*, 10546–10551.
- (10) Bashir, A.; Käfer, D.; Müller, J.; Wöll, C.; Terfort, A.; Witte, G. Selenium as a Key Element for Highly Ordered Aromatic Self-Assembled Monolayers. *Angew. Chem., Int. Ed.* **2008**, *47*, S250–S253.
- (11) Cyganik, P.; Szelagowska-Kunstman, K.; Terfort, A.; Zharnikov, M. Odd-Even Effect in Molecular Packing of Biphenyl-Substituted Alkaneselenol Self-Assembled Monolayers on Au(111): Scanning Tunneling Microscopy Study. *J. Phys. Chem. C* **2008**, *112*, 15466–15473.
- (12) Dendzik, M.; Terfort, A.; Cyganik, P. Odd-even Effect in the Polymorphism of Self-Assembled Monolayers of Biphenyl-Substituted Alkaneselenolates on Au(111). *J. Phys. Chem. C* **2012**, *116*, 19535–19542.
- (13) Cyganik, P.; Buck, M.; Wilton-Ely, J. D.; Wöll, C. Stress in Self-Assembled Monolayers: ω -biphenyl Alkane Thiols on Au(111). *J. Phys. Chem. B* **2005**, *109*, 10902–10908.
- (14) Ossowski, J.; Wächter, T.; Silies, L.; Kind, M.; Noworolska, A.; Blobner, F.; Gnatek, D.; Rysz, J.; Bolte, M.; Feulner, P.; Terfort, A.; Cyganik, P.; Zharnikov, M. Thiolate versus Selenolate: Structure, Stability and Charge Transfer Properties. *ACS Nano* **2015**, *9*, 4508–4526.
- (15) Cometto, F. P.; Patrino, E. M.; Paredes Olivera, P.; Zampieri, G.; Ascolani, H. Electrochemical, High-Resolution Photoemission Spectroscopy and vdW-DFT Study of the Thermal Stability of Benzenethiol and Benzeneselenol Monolayers on Au(111). *Langmuir* **2012**, *28*, 13624–13635.
- (16) Sato, Y.; Mizutani, F. Formation and Characterization of Aromatic Selenol and Thiol Monolayers on Gold: In-Situ IR Studies and Electrochemical Measurements. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1328–1331.
- (17) Ossowski, J.; Rysz, J.; Krawiec, M.; Maciazek, D.; Postawa, Z.; Terfort, A.; Cyganik, P. Oscillations in the Stability of Consecutive Chemical Bonds Revealed by Ion-Induced Desorption. *Angew. Chem., Int. Ed.* **2015**, *54*, 1336–1340.
- (18) Ossowski, J.; Rysz, J.; Terfort, A.; Cyganik, P. Relative Stability of Thiolate and Selenolate SAMs on Ag(111) Substrate Studied by Static SIMS. Oscillation in Stability of Consecutive Chemical Bonds. *J. Phys. Chem. C* **2017**, *121*, 459–470.
- (19) Wyczawska, S.; Cyganik, P.; Terfort, A.; Lievens, P. Ion-Beam-Induced Desorption as a Method for Probing the Stability of the

Molecule-Substrate Interface in Self-Assembled Monolayers. *ChemPhysChem* **2011**, *12*, 2554–2557.

(20) Huang, F. K.; Horton, R. C.; Myles, D. C.; Garrell, R. L. Selenolates as Alternatives to Thiolates for Self-Assembled Monolayers: A SERS Study. *Langmuir* **1998**, *14*, 4802–4808.

(21) Yokota, K.; Taniguchi, M.; Kawai, T. Control of the Electrode-Molecule Interface for Molecular Devices. *J. Am. Chem. Soc.* **2007**, *129*, 5818–5819.

(22) Weidner, T.; Shaporenko, A.; Müller, J.; Hölting, M.; Terfort, A.; Zharnikov, M. Self-Assembled Monolayers of Aromatic Tellurides on (111)-Oriented Gold and Silver. *J. Phys. Chem. C* **2007**, *111*, 11627–11635.

(23) Szelagowska-Kunstman, K.; Cyganik, P.; Schüpbach, B.; Terfort, A. Relative Stability of Thiol and Selenol Based SAMs on Au(111) - Exchange Experiments. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4400–4406.

(24) Hohman, J. N.; Thomas, J. C.; Zhao, Y.; Auluck, H.; Kim, M.; Visselaar, W.; Kommeren, S.; Terfort, A.; Weiss, P. S. Exchange Reactions between Alkanethiolates and Alkaneselenols on Au{111}. *J. Am. Chem. Soc.* **2014**, *136*, 8110–8121.

(25) Moulder, J. F.; Stickle, W. E.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photo-electron Spectroscopy*; Perkin-Elmer Corp.: Eden Prairie, MN, 1992.

(26) Kondoh, H.; Nakai, I.; Nambu, A.; Ohta, T.; Nakamura, T.; Kimura, R.; Matsumoto, M. Dissociative and Non-Dissociative Adsorption of Selenophene on Au(111) Depending on the Preparation Method. *Chem. Phys. Lett.* **2001**, *350*, 466–472.

(27) Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M. Ab Initio Molecular Simulations with Numeric Atom-Centered Orbitals. *Comput. Phys. Commun.* **2009**, *180*, 2175–2196.

(28) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *629*, 453–462.

(29) Tkatchenko, A.; Scheffler, M. Accurate Molecular van der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Phys. Rev. Lett.* **2009**, *102*, 073005.

(30) Freysoldt, C.; Eggert, P.; Rinke, P.; Schindlmayr, A.; Scheffler, M. Screening in Two Dimensions: GW Calculations for Surfaces and Thin Films Using the Repeated-Slab Approach. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *77*, 235428.

(31) Ruiz, V. G.; Liu, W.; Zojer, E.; Scheffler, M.; Tkatchenko, A. Density-Functional Theory with Screened van der Waals Interactions for the Modeling of Hybrid Inorganic-Organic Systems. *Phys. Rev. Lett.* **2012**, *108*, 146103.

(32) Neugebauer, J.; Scheffler, M. Adsorbate-Substrate and Adsorbate-Adsorbate Interactions of Na and K Adlayers on Al(111). *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 16067.

(33) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.

(34) Lamont, C. L. A.; Wilkes, J. Attenuation Length of Electrons in Self-Assembled Monolayers of n-Alkanethiols on Gold. *Langmuir* **1999**, *15*, 2037–2042.

(35) Rading, D.; Kersting, R.; Benninghoven, A. Secondary Ion Emission from Molecular Overlayers: Thiols on Gold. *J. Vac. Sci. Technol., A* **2000**, *18*, 312–319.

(36) Cooper, E.; Leggett, G. Static Secondary Ion Mass Spectrometry Studies of Self-Assembled Monolayers: Influence of Adsorbate Chain Length and Terminal Functional Group on Rates of Photooxidation of Alkanethiols on Gold. *Langmuir* **1998**, *14*, 4795–4801.

(37) Tarlov, M. J.; Newman, J. G. Static Secondary Ion Mass Spectrometry of Self-Assembled Alkanethiol Monolayers on Gold. *Langmuir* **1992**, *8*, 1398–1405.

(38) Arezki, B.; Delcorte, A.; Chami, A. C.; Garrison, B. J.; Bertrand, P. Gold-Thiolate Cluster Emission from SAMs under keV Ion Bombardment: Experiments and Molecular Dynamics Simulations. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2003**, *212*, 369–375.

(39) Arezki, B.; Delcorte, A.; Garrison, B. J.; Bertrand, P. Understanding Gold-Thiolate Cluster Emission from Self-assembled Monolayers upon Kilolectronvolt Ion Bombardment. *J. Phys. Chem. B* **2006**, *110*, 6832–6840.

(40) Nie, H. Y. Revealing Different Bonding Modes of Self-Assembled Octadecylphosphonic Acid Monolayers on Oxides by Time-of-Flight Secondary Ion Mass Spectrometry: Silicon vs Aluminum. *Anal. Chem.* **2010**, *82*, 3371–3376.

(41) Zhou, C.; Jones, J. C.; Trionfi, A.; Hsu, J. W. P.; Walker, A. Electron Beam-Induced Damage of Alkanethiolate Self-Assembled Monolayers Adsorbed on GaAs (001): A Static SIMS Investigation. *J. Phys. Chem. C* **2010**, *114*, 5400–5409.

(42) Redhead, P. A. Thermal Desorption of Gases. *Vacuum* **1962**, *12*, 203–211.

(43) Stettner, J.; Winkler, A. Characterization of Alkanethiol Self-Assembled Monolayers on Gold by Thermal Desorption Spectroscopy. *Langmuir* **2010**, *26*, 9659–9665.

(44) Käfer, D.; Witte, G.; Cyganik, P.; Terfort, A.; Wöll, C. A Comprehensive Study of Self-Assembled Monolayers of Anthracene Thiol on Gold: Solvents Effects, Structure and Stability. *J. Am. Chem. Soc.* **2006**, *128*, 1723–1732.

(45) Track, A. M.; Rissner, F.; Romaner, L.; Käfer, D.; Bashir, A.; Rangger, G. M.; Hofmann, O. T.; Bučko, T.; Witte, G.; Zojer, E. Simultaneously Understanding the Geometric and Electronic Structure of Anthraceneselenolate on Au(111): A Combined Theoretical and Experimental Study. *J. Phys. Chem. C* **2010**, *114*, 2677–2684.

(46) Forster-Tonigold, K.; Groß, A. A Systematic DFT Study of Substrate Reconstruction Effects due to Thiolate and Selenolate Adsorption. *Surf. Sci.* **2015**, *640*, 18–24.

(47) Kondoh, H.; Kodama, C.; Sumida, H.; Nozoye, H. Molecular Processes of Adsorption and Desorption of Alkanethiol Monolayers on Au(111). *J. Chem. Phys.* **1999**, *111*, 1175–1184.

(48) Hayashi, T.; Wakamatsu, K.; Ito, E.; Hara, M. Effect of Steric Hindrance on Desorption Processes of Alkanethiols on Au(111). *J. Phys. Chem. C* **2009**, *113*, 18795–18799.

(49) Stettner, J.; Frank, P.; Griesser, T.; Trimmel, G.; Schennach, R.; Gilli, E.; Winkler, A. A Study on the Formation and Thermal Stability of 11-MUA SAMs on Au(111)/Mica and on Polycrystalline Gold Foils. *Langmuir* **2009**, *25*, 1427–1433.

(50) Voets, J.; Gerritsen, J. W.; Grimbergen, R. F. P.; van Kempen, H. Chain-Length-Dependent Structure of Alkanethiols Forming Dimers on Au(111). *Surf. Sci.* **1998**, *399*, 316–323.

(51) Turchanin, A.; El-Desawy, M.; Götzhäuser, A. High Thermal Stability of Cross-Linked Aromatic Self-Assembled Monolayers: Nanopatterning via Selective Thermal Desorption. *Appl. Phys. Lett.* **2007**, *90*, 053102.

(52) Turchanin, A.; Käfer, D.; El-Desawy, M.; Wöll, C.; Witte, G.; Götzhäuser, A. Molecular Mechanisms of Electron-Induced Cross-Linking in Aromatic SAMs. *Langmuir* **2009**, *25*, 7342–7352.

(53) Whelan, C. M.; Barnes, C. J.; Gregoire, C.; Pireaux, J. J. The influence of step sites on the bonding of benzenethiol on Au surfaces. *Surf. Sci.* **2000**, *454–456*, 67–72.

(54) Verwüster, E.; Hofmann, O. T.; Egger, D. A.; Zojer, E. Electronic Properties of Biphenylthiolates on Au(111): The Impact of Coverage Revisited. *J. Phys. Chem. C* **2015**, *119*, 7817–7825.

(55) Liu, W.; Tkatchenko, A.; Scheffler, M. Modeling Adsorption and Reactions of Organic Molecules at Metal Surfaces. *Acc. Chem. Res.* **2014**, *47*, 3369–3377.

(56) Ramalho, J. P. P.; Gomes, J. R. B.; Illas, F. Accounting for van Der Waals Interactions between Adsorbates and Surfaces in Density Functional Theory Based Calculations: Selected Examples. *RSC Adv.* **2013**, *3*, 13085–13100.

(57) Lavrich, D. J.; Wetterer, S. M.; Bernasek, S. L.; Scoles, G. Physisorption and Chemisorption of Alkanethiols and Alkyl Sulfides on Au(111). *J. Phys. Chem. B* **1998**, *102*, 3456–3465.

(58) Chandekar, A.; Sengupta, S. K.; Whitten, J. E. Thermal Stability of Thiol and Silane Monolayers: A Comparative Study. *Appl. Surf. Sci.* **2010**, *256*, 2742–2749.

(59) Götzhäuser, A.; Panov, S.; Schertel, A.; Mast, M.; Wöll, C.; Grunze, M. Growth of Pyromellitic Dianhydride on an Amino-Terminated Surface. *Surf. Sci.* **1995**, *334*, 235–247.

(60) Rufael, T. S.; Huntley, D. R.; Mullins, D. R.; Gland, J. L. Methyl Thiolate on Ni(II): Multiple Adsorption Sites and Mechanistic Implications. *J. Phys. Chem.* **1995**, *99*, 11472–11480.

(61) Cranton, G.; Heyding, R. The Gold/Selenium System and Some Gold Seleno-Tellurides. *Can. J. Chem.* **1968**, *46*, 2637–2640.